AD-A109 830   NAVAL RESEARCH LAB WASHINGTON DC   F/G 14/2

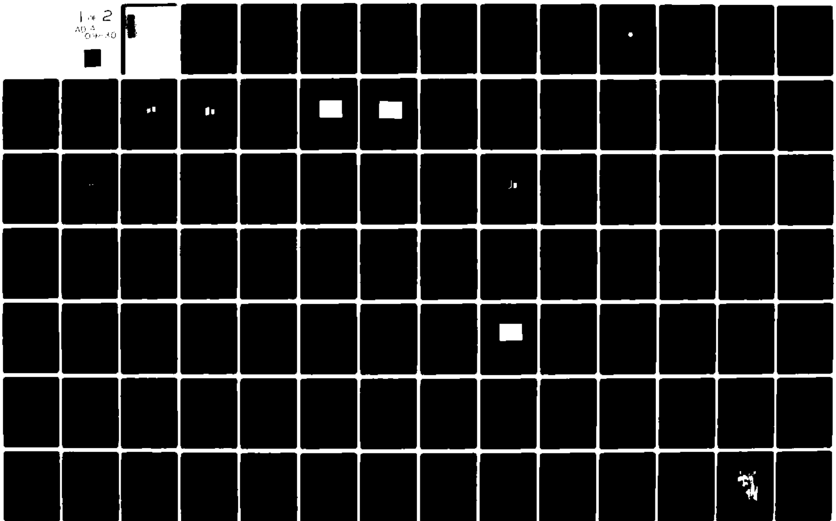
A TECHNIQUE TO MEASURE THE VOLUME OF ELASTOMERS AS A FUNCTION O--ETC(U)

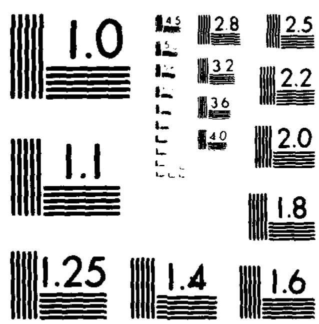
DEC 81 E K HOLMSTROM, A J RUDGERS

UNCLASSIFIED NRL-MR-4584   NL

1 of 2

AD A
109830





MICROCOPY RESOLUTION TEST CHART

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER NRL Memorandum Report 4584	2. GOVT ACCESSION NO. AD-A109 830	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A TECHNIQUE TO MEASURE THE VOLUME OF ELASTOMERS AS A FUNCTION OF TEMPERATURE AND PRESSURE WITH AN ACOUSTIC PYCNOMETER		5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL problem. 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Erik N. Holmstrom and Anthony J. Rudgers		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Underwater Sound Reference Detachment Naval Research Laboratory P. O. Box 8337, Orlando, FL 32856		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N-11; RR011-08-42; 0585-0-0
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375		12. REPORT DATE December 28, 1981 13. NUMBER OF PAGES 106
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Volume determination of elastomers
Static bulk modulus
Isothermal bulk modulus
Dynamic bulk modulus
Acoustic pycnometer
Acoustic densitometer
Properties of elastomers
Mechanical properties of rubber

(Continues)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A technique to determine the volume of elastomer samples as a function of temperature and pressure is described. The volume of butyl-252 elastomer sample is measured with an acoustic pycnometer at temperatures of 10°C and 25°C over the pressure range from 2 MPa to 70 MPa with an accuracy of better than 0.3 percent. A calibration method is used to enhance the low-pressure range of the acoustic pycnometer. The theory is developed for this calibration procedure.

(Continues)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. Key Words (Continued)

Neoprene type-W
Butyl-252
Rational fractions
Least-squares curve fit
P-V-T apparatus
Acoustic Rayleigh scattering
Ultrasonic distance measurement

20. Abstract (Continued)

From the volume vs. pressure measurements, the isothermal bulk modulus is calculated at 10°C and 25°C for the butyl-252 sample. The volume of a type-W neoprene elastomer sample is also measured at 25°C over the indicated pressure range.

CONTENTS

A TECHNIQUE TO MEASURE THE VOLUME OF ELASTOMERS AS A FUNCTION OF TEMPERATURE AND PRESSURE WITH AN ACOUSTIC PYCNOMETER

I. INTRODUCTION

This report describes the use of an acoustic pycnometer to measure the volume of a spherical elastomer sample as a function of temperature and pressure. The measurement of the volume of elastomer samples is needed in determining the bulk modulus of elastomers.

The bulk modulus of a material is defined as the ratio of a tensile or compressive stress, triaxial and equal in all directions (e.g., hydrostatic pressure), [1] to the relative change in volume it produces. For a spherical sample this triaxial compressive stress is depicted as a squeezing of the spherical sample by hydrostatic pressure, in which a change in volume occurs without a change in shape (See Fig. 1) [2]. The static bulk modulus is defined as

$$B(P,T) = -\frac{\Delta P}{\Delta V/V_s(P,T)}, \tag{1}$$

where

$B(P,T)$ = the static bulk modulus at pressure P and temperature T.

ΔV = the change in volume of the sphere

$V_s(P,T)$ = the volume of the spherical sample at P and T.

To calculate the static or isothermal bulk modulus using Eq. (1), a precise method to measure the volume of the sample $V_s(P,T)$ and correspondingly the change in volume of the sample ΔV is needed.

Manuscript submitted August 14, 1981.

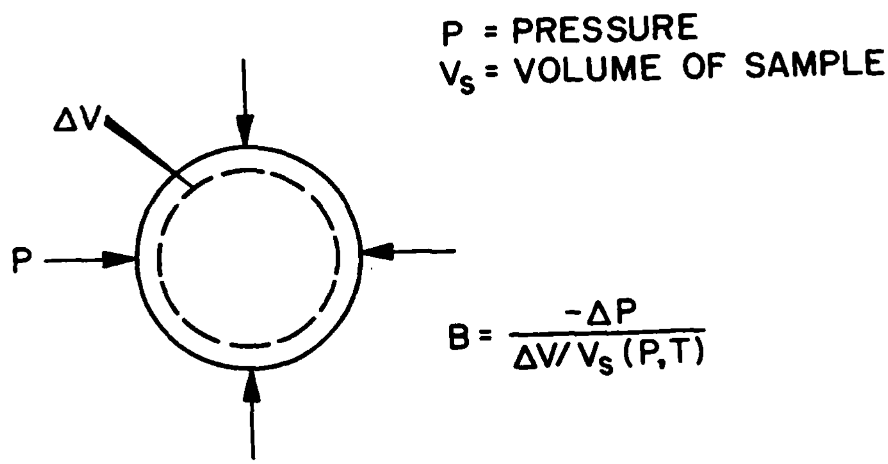


Fig. 1 — Description of bulk modulus B

The dynamic bulk modulus of a material can be defined as the ratio of a harmonically varying acoustic pressure to the corresponding change in volume it produces, multiplied by the volume of the sample of the material at the appropriate static pressure P and temperature T. The expression for the dynamic bulk modulus of the sphere in Fig. 1 is

$$K(P,T,f) = -\frac{p(f)}{\Delta v/V_s(P,T)}, \tag{2}$$

where

$K(P,T,f)$ = the dynamic bulk modulus of the sphere at static pressure P, temperature T, and frequency f

p = the varying uniform acoustic pressure with frequency f

Δv = the change in volume of the sphere due to the acoustic pressure p.

Persons who work in the field of hydroacoustics are interested in the dynamic bulk modulus of elastomers. Elastomers are used in transducers to isolate the electrical components from seawater. Another application of elastomers in hydroacoustics, is in their use as hull coatings on submarines. Therefore, a precise experimental method to determine the dynamic bulk modulus is of importance. One way to obtain an expression for the dynamic bulk modulus of an elastomer sample is from the theory describing the scattering of sound by an elastic sphere. In brief, if one uses the theory for Rayleigh scattering as the basis for dynamic bulk-modulus determination, the following arguments apply.

An expression containing the dynamic bulk modulus of an elastomer is obtained by solving the boundary-value problem for the scattering of sound by an elastic sphere [3] composed of the elastomer that is immersed in a fluid. If one looks at the scattering of sound in a confined chamber where a volume-expander sound source (shown in Fig. 2) produces a harmonic, uniform acoustic pressure, then the expression for the scattered pressure is

$$p_s = -\frac{p_i k_3^3 a_e^2}{3r}\left(1 - \frac{K_f}{K_e}\right) , \tag{3}$$

where

p_s = the scattered acoustic pressure

p_i = the incident acoustic pressure

k_3 = $2\pi f/c_3$, the wave number in the fluid

c_3 = the speed of sound in the fluid

a_e = the radius of the spherical elastomer

K_f = the dynamic bulk modulus of the fluid

K_e = the dynamic bulk modulus of the spherical elastomer

r = the distance from the center of the spherical elastomer to the receiver.

Equation (3) is true for nearfield ($k_3 r < 1$) Rayleigh scattering ($k_3 a_e << 1$) of the zero mode. The zero mode is the first term in the series expansion of the solution to the boundary-value problem and physically represents a uniform acoustic pressure field or breathing

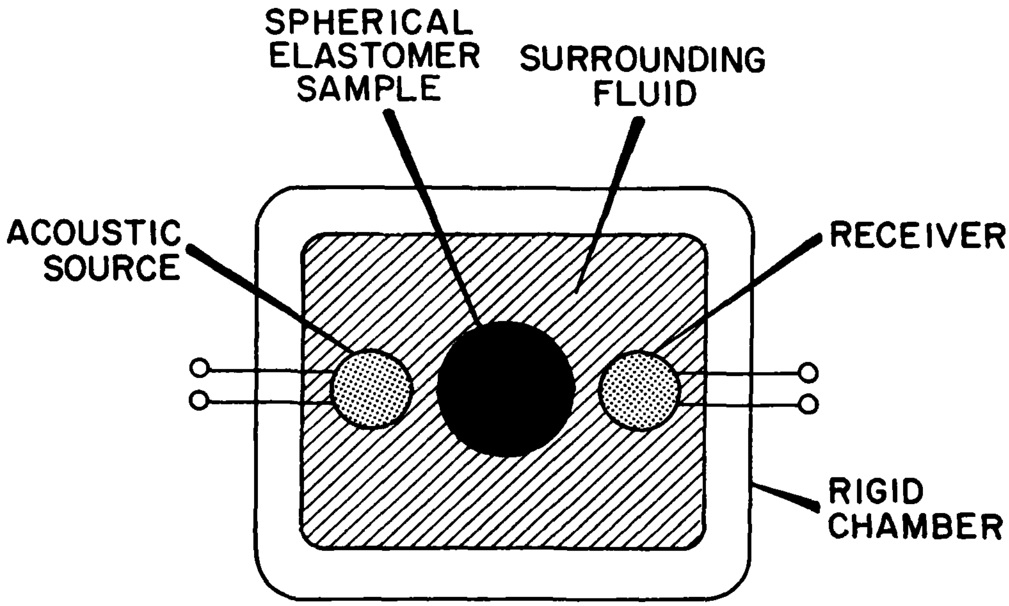


Fig. 2 — Scattering of sound by a spherical elastomer sample in a confined chamber

mode. The breathing mode is the mode of vibration that corresponds to a harmonically varying hydrostatic pressure. If the chamber is sufficiently small, only the zero mode is present.

If an acoustic scattering experiment is performed as shown in Fig. 2, the scattered pressure is not measured directly. The total pressure is measured by the receiver and is given by the expression

$$p_{total} = p_i + p_s, \tag{4}$$

where

$$p_{total} = \text{the total pressure.}$$

An expression for the ratio of K_f/K_e in the confined chamber in Fig. 2 can be obtained if three measurements are made: a measurement with the chamber filled only with fluid, a measurement with a spherical elastomer sample present in the fluid-filled chamber, and a measurement with a rigid scatterer present in the fluid-filled chamber. By measuring the total pressure p_{total} with no sample present in the chamber, the incident pressure expressed by Eq. (4) can be found. In any nearfield experiment, the distance r from point of observation to the sample must be taken into account. This is accomplished by introducing the expression for the scattered pressure for a rigid sphere when placed in the same position in the confined chamber in Fig. 2. The expression [4] for the scattered pressure for a rigid sphere is

$$p_{r,s} = -\frac{p_i k_3^2 a_r^3}{3r} \tag{5}$$

where

$p_{r,s}$ = the scattered pressure from a rigid sphere

a_r = the radius of the rigid sphere.

Using Eqs. (3), (4), and (5), one can obtain expressions for the total acoustic pressures for scattering by a spherical elastomer sample and by a rigid sphere in the confined chamber in Fig. 2. The results are

$$p_{t,e} = p_i \left\{ 1 - \frac{k_3^2 a_e^3}{3r} \left(1 - \frac{K_f}{K_e}\right) \right\} \tag{6a}$$

and

$$p_{t,r} = p_i \left\{ 1 - \frac{k_3^2 a_r^3}{3r} \right\}, \tag{6b}$$

where

$p_{t,e}$ = the total pressure measured when a spherical elastomer sample is present in the confined chamber

$p_{t,r}$ = the total pressure measured when a rigid sphere is present in the confined chamber.

The ratio of the bulk modulus of the fluid to the bulk modulus of the spherical elastomer sample is obtained by combining the results given in Eqs. (3), (4), and (6), assuming that p_i is the same:

$$\frac{K_f}{K_e} = 1 - \frac{V_r}{V_e} \left\{ \frac{1 - \frac{p_{t,e}}{p_i}}{1 - \frac{p_{t,r}}{p_i}} \right\} , \qquad (7)$$

where

V_r = the volume of the rigid sphere

V_e = the volume of the spherical elastomer sample.

Equation (7) expresses the ratio of the dynamic bulk modulus of the fluid in the confined chamber (refer to Fig. 2) to the dynamic bulk modulus of the spherical elastomer in the chamber. To calculate the ratio K_f/K_e, using Eq. (7), as a function of temperature and pressure, the volume V_e of the spherical elastomer sample must be known as a function of temperature and pressure. A confined chamber is analyzed because one is interested in determining the ratio K_f/K_e as a function of pressure and temperature. The chamber shown in Fig. 2 permits one to simulate the effect of ocean pressures.

The volume of a spherical elastomer sample can be measured accurately by means of an acoustic pycnometer. The background for the acoustic pycnometer used evolved from the work of Corsaro, Jarzynski, and Davis [5]. These investigators describe the use of an acoustic densitometer to measure the change in volume of polyethylene oxide as a function of temperature and pressure with a precision of 3 parts in 10^5.

$$\frac{K_f}{K_e} = 1 - \frac{V_r}{V_e}\left\{\frac{1 - \frac{p_{t,e}}{p_i}}{1 - \frac{p_{t,r}}{p_i}}\right\}, \tag{7}$$

where

V_r = the volume of the rigid sphere

V_e = the volume of the spherical elastomer sample.

Equation (7) expresses the ratio of the dynamic bulk modulus of the fluid in the confined chamber (refer to Fig. 2) to the dynamic bulk modulus of the spherical elastomer in the chamber. To calculate the ratio K_f/K_e, using Eq. (7), as a function of temperature and pressure, the volume V_e of the spherical elastomer sample must be known as a function of temperature and pressure. A confined chamber is analyzed because one is interested in determining the ratio K_f/K_e as a function of pressure and temperature. The chamber shown in Fig. 2 permits one to simulate the effect of ocean pressures.

The volume of a spherical elastomer sample can be measured accurately by means of an acoustic pycnometer. The background for the acoustic pycnometer used evolved from the work of Corsaro, Jarzynski, and Davis [5]. These investigators describe the use of an acoustic densitometer to measure the change in volume of polyethylene oxide as a function of temperature and pressure with a precision of 3 parts in 10^5.

II. ACOUSTIC PYCNOMETER THEORY

The acoustic pycnometer* is an instrument which is used to precisely measure the volume of an elastomer sample. In this section the theory used in the acoustic pycnometer measurement is outlined. First, the principle of operation of the pycnometer is described. Second, the pertinent equations are derived.

The acoustic pycnometer, shown in Fig. 3a, is composed of a two-part Invar container, held together with screws and sealed with neoprene O-rings. Within the container there is a sample chamber connected to a bore by a narrow canal. At the base of the bore is an ultrasonic quartz transducer. The transducer is a resonant device, which is 1.905 cm in diameter, 0.75 cm in thickness and operates at a frequency of 4 MHz. The entire pycnometer is filled with mercury (shown in black in Fig. 3a) under vacuum. The sound path, in the bore of the pycnometer, is terminated by a resonant float to flatten the mercury meniscus. The float design will be discussed later.

----

*The acoustic densitometer of Corsaro, Jarzynski, and Davis was obtained from the Naval Research Laboratory in Washington, DC, but because of its existing condition was unusable when this research was undertaken. Several modifications had to be made in order to use it. Because of these extensive modifications and because the modified device was used in a different way than by Corsaro, Jarzynski, and Davis, its name was changed to the acoustic pycnometer to distinguish it from the original densitometer. The new name is appropriate because a pycnometer is an instrument used to measure the volume or the density of a material. On the other hand, the word "densitometer" might imply a connection with the kind of instrument used in photography when there is none.

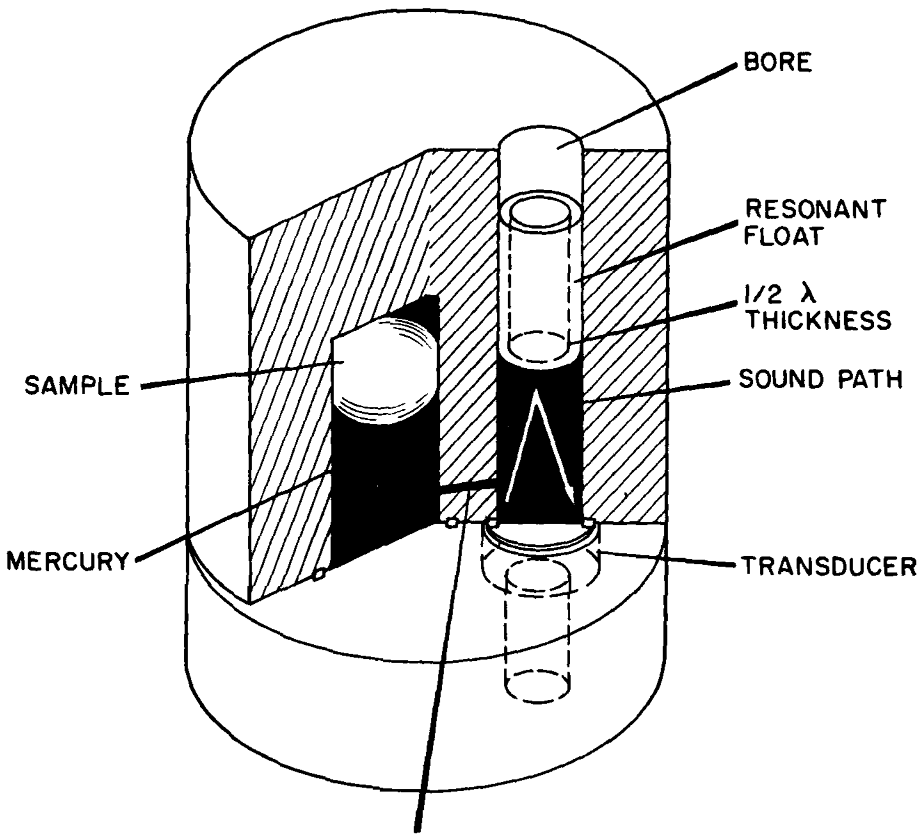


Fig. 3a — Acoustic pycnometer with a spherical sample present

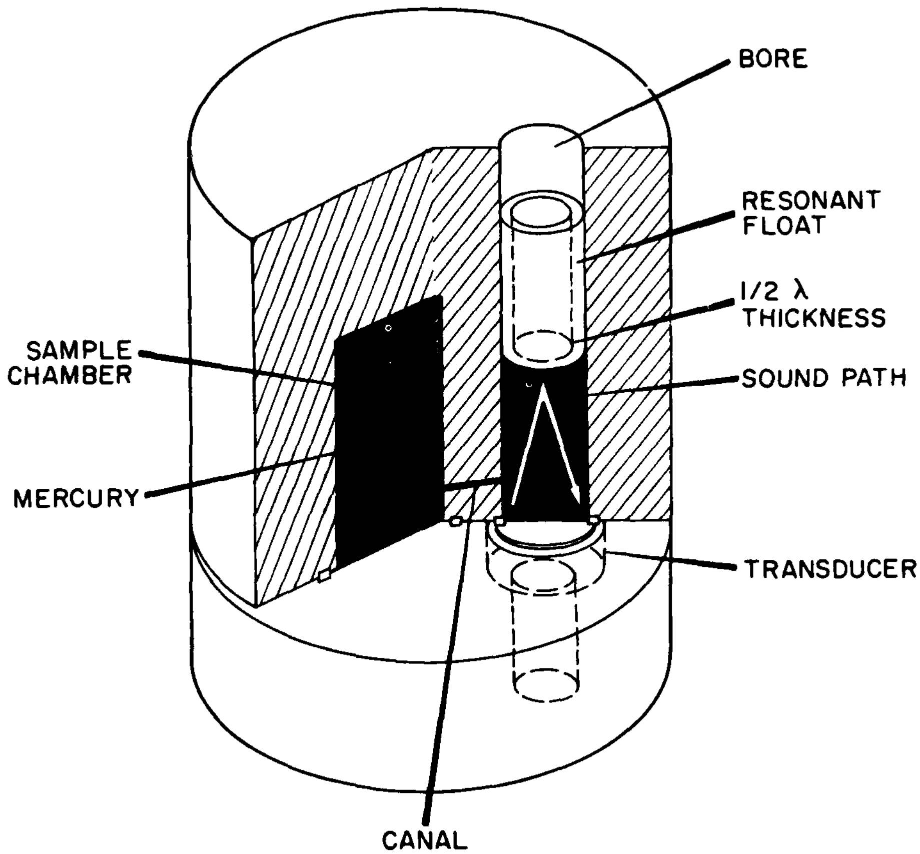


Fig. 3b — Acoustic pycnometer: calibration case

An electronically generated 4-MHz pulse is used (see Fig. 4) to excite the transducer at the base of the bore of the pycnometer causing the transducer to transmit an ultrasonic 4-MHz pulse through the column of mercury in the bore. This pulse is reflected by the float and travels back through the column of mercury where the reflected pulse is received by the transducer and is also reflected by the transducer back into the mercury-filled column. The process repeats, producing a sequence of echoes, until an electronically controlled repetition time has elapsed and another pulse is generated by the electronic equipment. This electronic pulse excites the transducer, and another transmitted pulse is produced at the transducer. Again a series of pulse echoes occurs. This series of pulse echoes is commonly called an echo train. Figure 5 is a photograph taken of an oscilloscope display of an echo train.

When a sample is placed in the sample chamber of the pycnometer (see Fig. 3a), the change in volume of the sample caused by any change in temperature and pressure produces a change in the volume of the mercury in the bore. The height of the mercury column is determined as follows. The time it takes for a 4-MHz sound pulse to travel from the transducer in the base of the bore through the mercury column to the float and return to the transducer is measured. This time is called the time-of-flight. This time-of-flight is determined by measuring the difference in time between two successive pulse echoes on an oscilloscope (as shown in Fig. 4). By multiplying the time-of-flight by the speed of sound in mercury, the length of the mercury column for any temperature

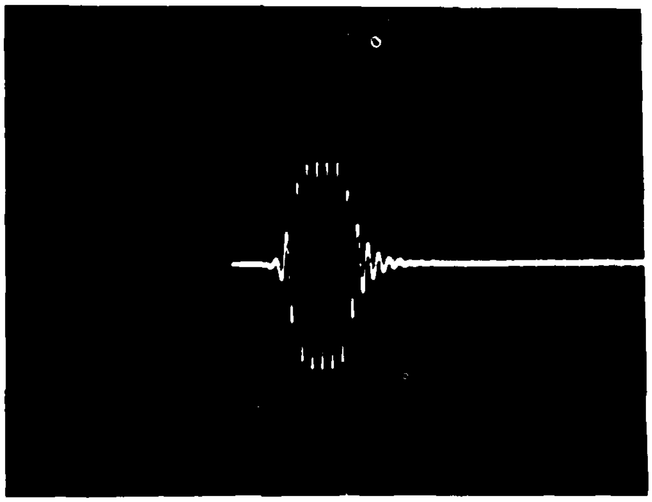


Fig. 4 — 4 MHz driving pulse, timebase = 2 μs
Pulse amplitude = 600 volts, peak-to-peak

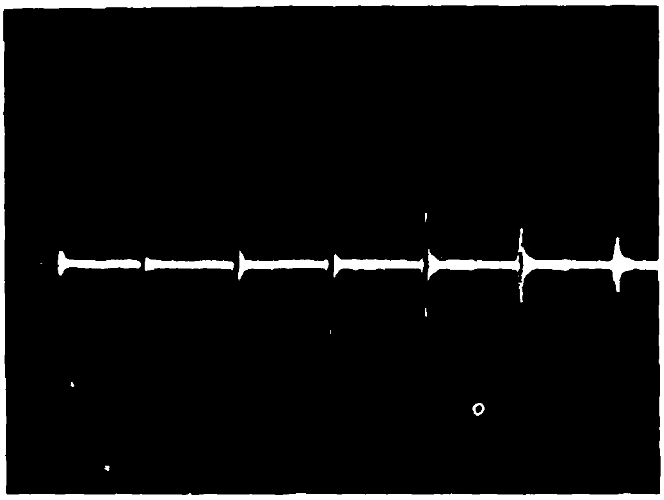


Fig. 5 — Pulse-echo train, timebase = 50 μs amplitude of the first echo in the train is approximately = 0.8 volts peak-to-peak.

and pressure can be calculated by

$$L = \frac{1}{2} c_{Hg} t_d , \tag{8}$$

where

L = the length of the mercury column

c_{Hg} = the speed of sound in mercury

t_d = the difference in time between two successive pulse-echoes.

The measurement of the time-of-flight will be discussed in detail in Appendix A. The volume of the mercury in the bore of the pycnometer is found by multiplying the length given by Eq. (8) by the cross-sectional area of the bore. The measured volume V_{BORE} is corrected to account for the change in dimension of the bore produced by changes in pressure and temperature. The volume of the mercury in the bore is given by

$$V_{BORE} = \frac{1}{2} c_{Hg} t_d \pi r_b^2 \exp[2(\alpha_V T - \beta_V P)/3], \tag{9}$$

where

r_b = the radius of the bore

α_V = the volume coefficient of thermal expansion of the pycnometer material

β_V = the volume coefficient of isothermal compressibility of the pycnometer material.

The units of the temperature and pressure are respectively in degrees C and MPa and the pressure used is gauge pressure. These units for temperature and pressure will be used throughout this paper. Equation (9) is derived in Appendix C.

Mercury is used as a working medium in the acoustic pycnometer because the speed of sound and compressibility of this liquid are well documented. The equation for the speed of sound in mercury as a function of temperature and pressure is [6]

$$c_{Hg}(P,T) = 1460.0 - 0.460T + 0.210P. \tag{10}$$

The units of the sound speed in Eq. (10) are m/s. The volume of an elastomer sample can be calculated if the volume of mercury in the bore is determined in two cases: a measurement is made with a sample present in the sample chamber of the pycnometer (shown in Fig. 3a) and a second measurement with no sample present in the sample chamber (see Fig. 3b). The measurements taken with no sample present in the pycnometer are referred to as a calibration run. A calibration method is used to account for the compressibility of the pycnometer, which is a significant effect in the experiment.

To obtain an expression for the volume of a sample when using the acoustic pycnometer, two cases must be analyzed: the calibration run and the sample run. Writing down the equations for the volumes of mercury in the pycnometer, in the configuration shown respectively

in Figs. 3a and 3b, one obtains

$$V_{Hg}(P,T) = V_{CHAM} + V_{CANAL} + V_{BORE} - V_{SAMPLE} \tag{11a}$$

and

$$V'_{Hg}(P,T) = V_{CHAM} + V_{CANAL} + V'_{BORE} \quad , \tag{11b}$$

where

$V_{Hg}(P,T)$ = the volume of mercury in the pycnometer during the sample run

$V'_{Hg}(P,T)$ = the volume of mercury in the pycnometer during the calibration run

V_{CHAM} = the volume of the chamber

V_{CANAL} = the volume of mercury in the canal

V_{BORE} = the volume of mercury in the bore during the sample run

V'_{BORE} = the volume of mercury in the bore during the calibration run

V_{SAMPLE} = the volume of the sample.

To obtain an expression for the volume of the sample, one subtracts Eq. (11b) from Eq. (11a). The result is

$$V_{SAMPLE} = V_{BORE} - V'_{BORE} + \frac{m' - m}{\rho_{Hg}(T_f)} \quad , \tag{12}$$

where

m' = the mass of mercury used in the pycnometer during the calibration run

m = the mass of mercury used in the pycnometer during the sample run

$\rho_{Hg}(T_f)$ = the density of mercury at the filling temperature T_f and the filling pressure P_f.

In Eq. (12) the difference $V_{Hg}' - V_{Hg}$ in the volumes of mercury in the pycnometer, which arose from the subtraction of Eq. (11b) from Eq. (11a), has been replaced by the difference in the masses of mercury divided by the density of mercury. The difference in V_{BORE} and V_{BORE}' at a given temperature T and pressure P is due to the change in volume of the sample and to filling the pycnometer with mercury to different heights during the sample run and during the calibration run. Therefore,

$$V_{BORE}(P,T) = V_{HgB} + \Delta V_{SAMPLE} , \tag{13a}$$

where

$V_{HgB}(T_f)$ = the volume of the mercury in the bore at temperature T_f and pressure P_f

ΔV_{SAMPLE} = the change in volume of the sample.

V_{BORE}' is equal to V_{BORE} plus a volume of mercury due to filling the bore of the pycnometer to a different height:

$$V_{BORE}'(P,T) = V_{HgB} + V(P,T) , \tag{13b}$$

where

$V(P,T)$ = the additional volume of mercury in the bore due to filling the pycnometer to different heights during the sample run and during the calibration run.

The difference in V_{BORE} and V'_{BORE} is obtained by subtracting Eq. (13a) from Eq. (13b). The result is

$$V_{BORE}(P,T) - V'_{BORE}(P,T) = V_{SAMPLE}(P,T) - V_{SAMPLE}(P_o,T_o) - V(P,T), \tag{14a}$$

where

$V_{SAMPLE}(P_o,T_o)$ = the initial volume of the sample when it is placed into the pycnometer (as measured by Archimedes' principle) at temperature T_o and ambient pressure P_o.

It should be noted that the pressures P_f and P_o both refer to ambient atmospheric pressure. Also the temperatures T_o and T_f were both approximately 25°C. By rearranging Eq. (14a), one obtains an expression for the volume of a sample as a function of pressure and temperature:

$$V_{SAMPLE}(P,T) = V_{SAMPLE}(P_o,T_o) + V_{BORE}(P,T) - V'_{BORE}(P,T) + V(P,T). \tag{14b}$$

Before Eq. (14b) can be used, an expression is needed for $V(P,T)$ in terms of known or measured quantities. This expression is found in

the following way. At the pressure P_o and the temperature T_o, Eqs. (12) and (14b) when subtracted give

$$V(P_o,T_o) = \frac{m' - m}{\rho_{Hg}(P_o,T_o)} - V_{SAMPLE}(P_o,T_o). \tag{15}$$

Equation (15) expresses the difference between the volumes of the mercury contained in the bore of the pycnometer during the calibration run and during the sample run at temperature T_o and pressure P_o. As mentioned earlier, the sample volume $V_{SAMPLE}(P_o,T_o)$ in Eq. (15) is determined by Archimedes' principle at ambient temperature T_o and pressure P_o, before being placed into the acoustic pycnometer. By using Eq. (15) and the equation of Grindley and Lind [7], which gives the volume of mercury as a function of temperature and pressure, one obtains for V(P,T) the expression

$$V(P,T) = \frac{D(P,T)}{D(P_o,T_o)} \left[\frac{m' - m}{\rho_{Hg}(T_o)} - V_{SAMPLE}(P_o,T_o) \right], \tag{16}$$

where

$$D(P,T) = 1 + d_1T - d_2P - d_3TP + d_4P^2 + d_5TP^2$$

$$d_1 = 1.821 \times 10^{-4}$$

$$d_2 = 3.153 \times 10^{-5}$$

$$d_3 = 5.19 \times 10^{-8}$$

$$d_4 = 4.54 \times 10^{-9}$$

$$d_5 = 1.19 \times 10^{-11}.$$

From the previous development of the theory, it can be seen that the volume of a sample can be determined as a function of temperature and pressure by Eqs. (14b) and (16). By using the calibration method, the compressibility of the pycnometer can be taken into account. Previous investigators attributed the compressibility of the pycnometer to be due solely to the compressibility of the Invar container material acting as a monolithic block of material. The calibration method requires accurate measurement of the initial sample volume prior to being inserted into the sample chamber of the pycnometer. This technique also requires accurate determination of the amounts of mercury used in the pycnometer during the calibration run and during the sample run. However, all of the measurements necessary for the success of the calibration method are made by standard laboratory procedures.

III. ACOUSTIC PYCNOMETER EXPERIMENTAL METHOD

The acoustic pycnometer can be used to determine the volume of elastomers as a function of temperature and pressure after two preliminary steps have been completed. First, the spherical elastomer samples need to be fabricated. Second, one needs to obtain the initial volume of the samples at ambient pressure P_o and a known temperature T_o $V_{SAMPLE}(P_o,T_o)$.

The pycnometer is assembled, and the transducer is put into place. The assembled pycnometer is then placed in a vacuum chamber where it is

to be filled with mercury (see Fig. 6). The mercury filling is done by using a burette from which mercury is drained into the sample chamber of the pycnometer while the pycnometer is kept under vacuum. Previous investigators at our laboratory determined the volume of mercury drained into the pycnometer by reading the volume of mercury used from the graduated scale on the burette. In the more accurate method, used in this investigation, the mass of the mercury used in filling the pycnometer was determined by weighing and the tabular value of the density of mercury was used to calculate the volume of mercury [8]. The volume of the mercury placed into the pycnometer is calculated by

$$V_{Hg} = \frac{m_i - m_f}{\rho_{Hg}(T_f)} , \qquad (17)$$

where,

m_i = the mass of mercury contained in the burette prior to filling the pycnometer

m_f = the mass of mercury contained in the burette after the pycnometer has been filled.

The mass m_i in Eq. (17) is obtained by weighing an initial amount of mercury, which is then poured into the burette shown in Fig. 6. Once the pycnometer is completely filled, the remaining mass m_f of mercury in the burette is reweighed and the volume of the mercury in the pycnometer is calculated by Eq. (17). Since mercury vapor is extremely toxic, extreme caution was exercised when performing the mercury filling.

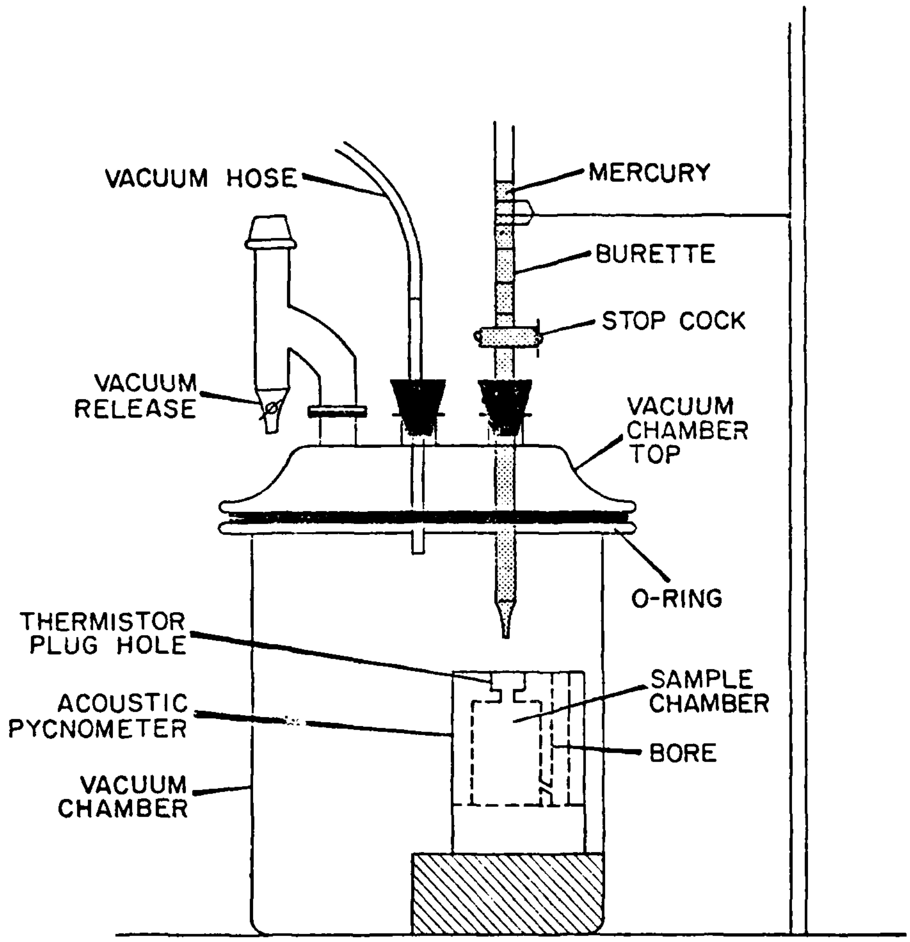


Fig. 6 — Mercury-filling apparatus

A major source of experimental error can occur when filling the acoustic pycnometer with mercury. Any mercury lost upon filling will result in an error when determining the amount of mercury in the acoustic pycnometer. For instance, a 0.2-cm^3 loss of mercury when filling the pycnometer, in the calibration run or sample run, would result in an error of 1.9 percent in determining the amount of mercury in the acoustic pycnometer. This error is significantly higher than the error experienced when the measurements were made. A second problem occurs when filling the pycnometer with mercury. Entrapped air is a major concern when using the acoustic pycnometer. Since the sample chamber is cylindrical in shape, if the pycnometer cell is not completely level when filling, air could be entrapped in the top of the sample chamber. To lessen the possibility of the entrapment of air, a conical sample chamber would seem to be a more logical design. If it has a conical shape, even if the sample chamber of the pycnometer is not level when the device is filled, air will not be trapped as easily.

After filling, the pycnometer is then ready to be interfaced with the electronic equipment by way of a waterproof-connector assembly called the electronics-interface module. This is shown in Fig. 7. The interface module and a teflon ring make the seal for the pressure vessel. The threaded pressure-vessel top acts as a backing for the interface module to compress the teflon ring so as to seal the pressure vessel. The interface module also acts as a feed-through to bring

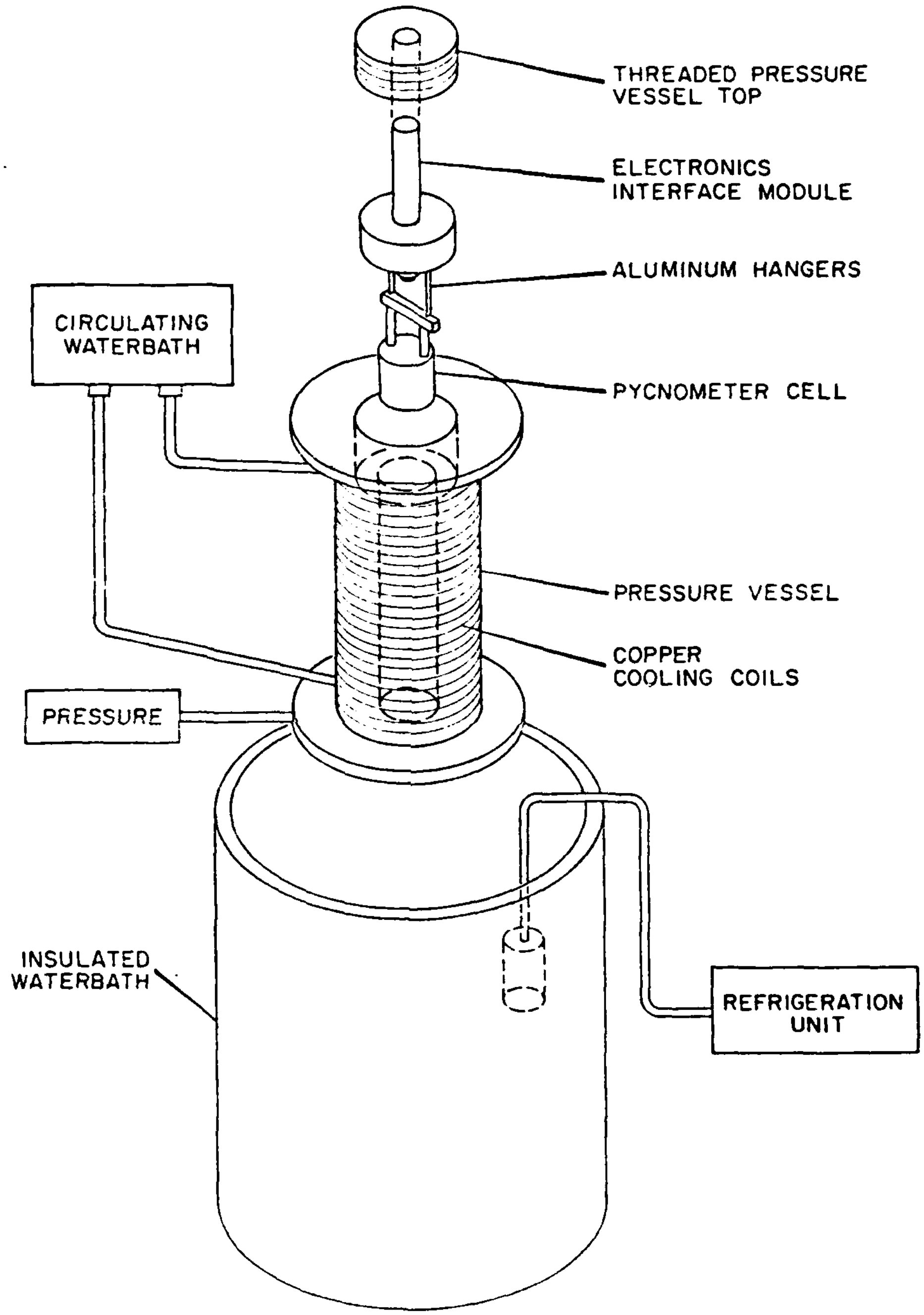


Fig. 7 — Pycnometer pressure and temperature control system

the electric wires from the pycnometer, inside the pressure vessel, out to the electronic equipment. The pressure vessel is placed into a large water bath for nominal temperature control. Precise temperature control is obtained by connecting a circulating bath to the copper coils surrounding the pressure vessel to maintain the pycnometer at the temperature desired. A pressure pump allows one to control the static pressure P to which the elastomer sample is subjected.

Pycnometer measurements are made as a function of pressure at constant temperature. When a desired temperature T is obtained at ambient pressure P_1, the volume of mercury in the bore is determined by the time-of-flight measurement described earlier. The pressure is now increased to some new value P_2 using the pump, and the temperature is allowed to return to T. After the temperature has stabilized, another time-of-flight measurement is made. This process is repeated at selected pressure values to 70 MPa, and then this process is reversed and measurements are made at the same pressure values back to ambient pressure. This constitutes a pressure cycle at temperature T. The selected pressures at which elastomer sample volume measurements were made were as follows: 0, 1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60, and 70 MPa. Finer pressure increments were used at low pressures (0 to 10 MPa) because the low-pressure behavior of the pycnometer was desired. Several of these pressure cycles at constant temperature were done for each of the volume measurement made during the calibration and sample runs.

The data obtained from the acoustic-pycnometer measurement are time-of-flight as a function of pressure at constant temperature. This time-of-flight is the time difference between two successive pulse echoes, shown in Fig. 5, and is equal to the round-trip time of flight in the bore. This time difference is measured by electronic means as a frequency which is the reciprocal of the time of flight of the sound pulse in the mercury column in the bore. A more detailed description of the electronic equipment is given in Appendix A.

The data from the acoustic-pycnometer measurements are processed in the sequence shown in Fig. 8. The pressure, temperature, and frequency data are entered into a Hewlett-Packard Model 9825 Calculator, which is used to compute the volumes of the mercury in the bore during the calibration and sample runs, using Eq. (9). These results are entered into a curve-fitting computer program RAGT.FTN on a PDP-11/45 computer, which is used to obtain an expression for the volume of the mercury in the bore as a function of pressure at constant temperature. The computer program RAGT.FTN uses the method of least-squares to fit an empirical expression to the data for the volume of the mercury in the bore, during the calibration run and the sample run. This empirical expression is needed to perform the sample-volume calculation using Eq. (14b). The computer program PYCNOM.FTN uses the results of the program, RAGT.FTN, to calculate the volume of the sample according to Eq. (14b). The results of these analyses are given in Section V. The programs RAGT.FTN and PYCNOM.FTN, are written in FORTRAN and make use of the PDP-11/45

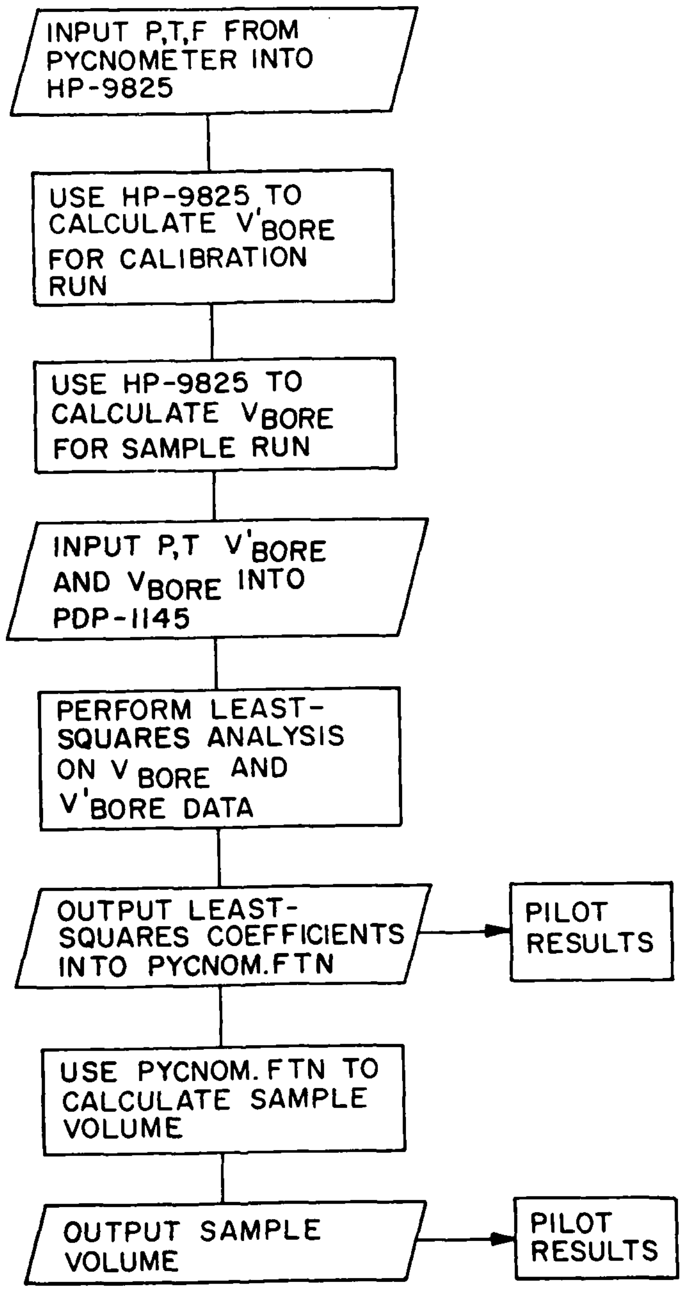


Fig. 8 — Acoustic-pycnometer data-processing flowchart

digital computer at the Naval Research Laboratory's Underwater Sound Reference Detachment (NRL-USRD). The computer programs used are given in Appendices C, D, and E.

IV. ENGINEERING CONSIDERATIONS

Volume measurements initially were attempted with an existing pycnometer previously tried by several experimenters. The acoustic pycnometer used in this investigation required several modifications before consistent experimental results were obtained. The major modifications were the construction of a thermistor plug, a transducer-crystal mount, and a resonant reflector float. These modifications were made as the need for each arose during the course of the experiment.

Figure 9 shows the acoustic densitomer of Corsaro, Jarzynski, and Davis [5]. These investigators encountered difficulties when making measurements at pressures below 7 MPa. They attributed their difficulties at low pressure to the presence of air in the sample chamber of the densitometer, which entered when the device was filled with mercury even though filling was carried out with the device in a vacuum chamber. Also in their design, the transducer in the base of the bore was backed with a spring to hold it tightly against the bottom of the bore so as to prevent mercury from leaking around the quartz crystal and shorting it out. Moreover, the float they used on top of the mercury meniscus in the bore was a cylinder with a conical top. The idea behind using the conical top on the float was to provide a tapered impedance so that

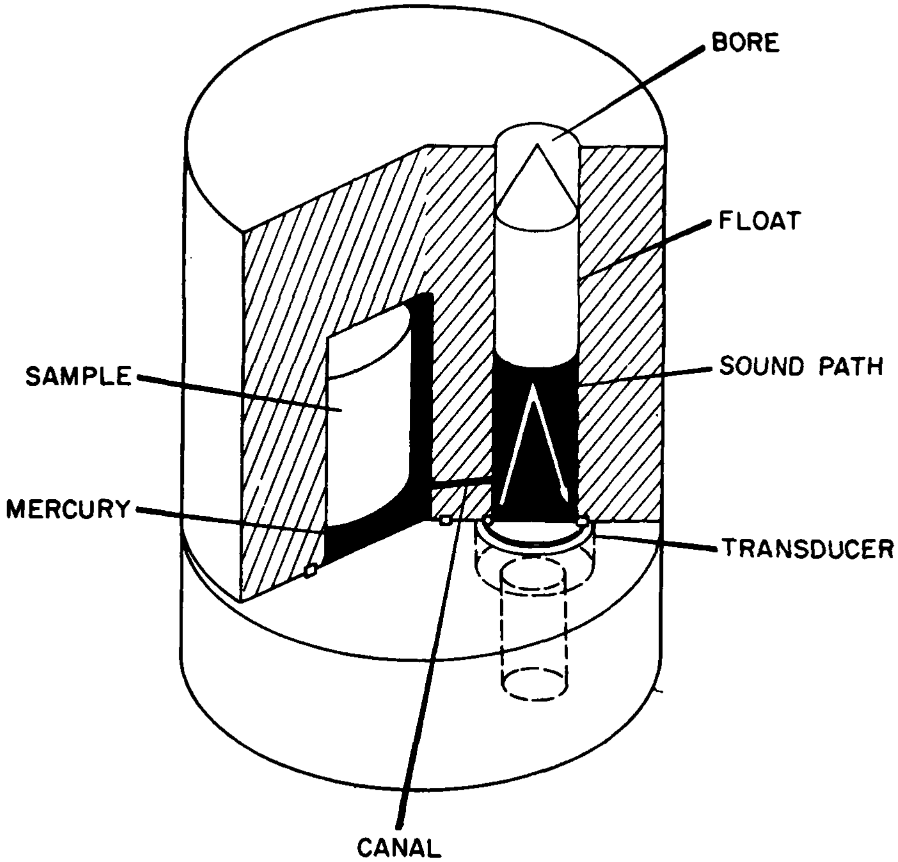


Fig. 9 — Acoustic densitometer

little, or no, reflection of the sound pulse would occur from the top of the float back into the mercury column. These investigators used a platinum resistance thermometer for monitoring the temperature in the pressure vessel. The theory Corsaro, Jarzynski, and Davis developed for the acoustic densitometer system took into account only the compressibility of the Invar container, as if it were a solid metal block, and of the mercury within the densitometer. No calibration of the system was performed to measure the behavior of the densitometer with the sample absent. A volume determination of a polyethylene-oxide sample was done by performing only a sample run. This neglected the possibility of experimentally determining the behavior of the densitometer as a function of temperature and pressure. In view of the significance of the effect determined in the experiment reported here, omitting the calibration procedure was a serious shortcoming in the technique of the earlier investigators.

Previous investigators at this laboratory replaced the platinum resistance thermometer used by Corsaro, Jarzynski, and Davis by two thermistors. One thermistor was located on the outside of the densitometer close to the Invar container. The second thermistor was placed inside the sample chamber of the densitometer, and the electrical leads were brought outside the sample chamber through a glass-to-metal seal. This glass-to-metal seal was screwed into the top of the densitomer directly above the sample chamber. The addition of the second thermistor assured that thermal equilibrium was attained when the two thermistors

were indicating the same value of temperature. When the existing acoustic densitometer was initially assembled and filled with mercury, it was observed that mercury was leaking around the screw threads of the glass-to-metal seal. This leak made the existing densitomer unusable. A thermistor plug was made to replace the glass-to-metal seal arrangement. This had a two-fold effect: thermal equilibrium could be assured because two thermistors were still used, and this thermistor plug provided a better way to fill the pycnometer with mercury. Previously, the densitometer was filled by draining mercury from a burette down into the bore where it landed on the quartz crystal. Sometimes this operation shattered the quartz transducer in the base of the bore. Filling in this way also permitted air to be trapped in the upper corners of the sample chamber. By pouring the mercury through the thermistor-plug hole, the sample chamber could be directly and completely filled with mercury. The thermistor plug is shown in Appendix G.

To ensure a better contact between the electrode and the quartz transducer crystal, an electrode plug was designed (see Appendix G) to mount the electrode and transducer at the base of the bore. This replaced the spring-backed transducer arrangement in the original acoustic densitometer. This transducer electrode plug was made of a machinable ceramic to hold the transducer electrode in place without shorting it out against the Invar container. An O-ring was used to make a seal between the transducer crystal and the electrode plug. Use of this electrode plug resulted in echoes of higher amplitude, a well-defined

baseline on the received signal with better quality pulse echoes, and more pulse echoes present in the echo train. The electrode plug also decreased the possibility of mercury flowing around the crystal and shorting out the electrode because of the O-ring seal used.

The float shown in Fig. 9 was replaced by the resonant float shown in Fig. 3a. When using the original conically topped float and observing the pulse echoes on an oscilloscope, one found that the baseline of the signal was not well defined, the amplitudes of the pulse echoes were not very large, and there were few echoes in the echo train. It appeared that this was due in part to an interference caused by the signals propagating through the float material and reflecting off the upper portion of the float. In the new design, this back-face reflection was used to advantage to enhance the received signal. A resonant float was made in the shape of a hollow cylinder, with the top open and the lower end having a thickness of one half the wavelength of the sound wave, in the material used for the float, at the driving frequency of 4 MHz. If the reflector is a half-wavelength thick, it permits the reflected signal from the inner surface of the cylindrical-float base to add in phase with the reflection from the base of the float. This increases the received signal amplitude and consequently makes the received signal more distinguishable from the baseline. The thickness necessary for the base of the float can be determined from the operating frequency of the transducer in the bore and the speed of sound in the material used for the float. The thickness is

$$d = \frac{1}{2} c_m / f \ , \tag{18}$$

where

d = the thickness desired for the base of the float

c_m = the speed of sound in the float material

f = the operating frequency of the transducer.

The float is made of stainless steel for which the bulk sound speed c_m = 5790 m/s. As stated earlier, the operating frequency is 4 MHz. Therefore, the desired thickness should be 0.072 cm or 0.028 in. It was found that this float-base thickness caused the reflected signal from the inner surface of the cylinder base to add up in phase with the reflected signal from the base of the float. This gave a well-defined baseline, an increased signal amplitude, and a greater number of pulse-echoes.

Additional problems arose with the existing densitometer due to the nature of the operating frequency and the high voltages encountered during the experiment. Electrical cross talk was abundant when the system was first used. Initially, a strain-gauge bridge with a pressure transducer was used to measure the static pressure in the system. The 4-MHz, cross-talk signal, which appeared on the pressure transducer wires, fed into the strain-gauge-bridge input terminals and continually burned them out. For this reason, a mechanical pressure gauge was substituted in lieu of the strain-gauge transducer and bridge.

This cross-talk signal also appeared on the thermistor leads, which in turn fed the signal into the electronic digital multimeters used to monitor the temperature by measuring the resistance of the thermistor. As a consequence, the multimeters were also being burned out. To solve this problem, several capacitors were placed in parallel across the inputs to the digital multimeters to short out the cross-talk signal before it entered the multimeters. These shorting capacitors would have no effect on the direct current that flowed through the thermistor. In addition, the pulse amplitude of the electronic system that generated the 4-MHz acoustic pulse was turned off when temperature readings were being made. Similarly, when the pulse amplitude was turned on during the time-of-flight measurement, the multimeters were turned off.

Once these modifications were made, the acoustic pycnometer could be used to determine the volume of elastomer samples.

V. EXPERIMENTAL RESULTS

The acoustic pycnometer was used to measure volume of two spherical elastomer samples approximately 2.5 cm in diameter. The two elastomer samples used were a sample of butyl-252 and a sample of type-W neoprene. The volumes of these elastomer samples were measured by Archimedes' principle at atmospheric pressure and 25°C before being placed into the sample chamber of the acoustic pycnometer. The volume of the sample of butyl-252 was 8.8433 cm^3, and the volume of the sample of type-W

neoprene was 8.7774 cm^3 at 25°C. A discussion of Archimedes' principle is given in Appendix E.

As stated earlier, the three measurements taken when using the acoustic pycnometer are frequency, pressure, and temperature. Frequency is the primary measurement necessary to obtain the time-of-flight through the mercury in the bore of the pycnometer. Pressure and temperature are auxiliary measurements. The frequency measurement can be made to two parts in 10^4. The precision in the pressure measurement and the temperature measurement is respectively ±0.1 MPa and ±0.2°C. A random-error analysis is given in Appendix B. The experimental results are calculated by computer and plotted on a Tektronix Model 4662 flat-bed plotter.

The acoustic pycnometer was calibrated at two temperatures (10°C and 25°C) and as a function of pressure (to 70 MPa). The pycnometer calibration runs are presented in Figs. 10 and 11. The points shown in the figures are the measured values for V'_{BORE}, the volume of the mercury in the bore, calculated using the HP-9825 program. The curves passing through the data points were determined by the curve-fitting routine, RAGT.FTN. Each had the form of a sixth-degree polynomial. The computer program RAGT.FTN determines an expression for the volume of the mercury in the bore as a function of pressure at constant temperature by the method of least squares. Data were taken on two pressure cycles at 10°C and 25°C. All of the calibration data for a given temperature ere analyzed together, and then the sixth-degree

polynomial was passed through the data. At pressures below 2 MPa, inconsistent results were obtained. This was apparent from the lack of precision observed in the data when measurements were made at low pressure. Also, the curve-fitting routine could not fit the measured values below 2 MPa. Therefore, all measured values below 2 MPa were discarded.

When the measurements were made in the case of the sample runs, the data for the volume of the mercury in the bore were analyzed cycle by cycle, when fitting the measured values to a sixth-degree polynomial. Again, two pressure cycles were taken at temperatures of 10°C and 25°C; but instead of lumping these data together and fitting a sixth-degree polynomial to all the data, a sixth-degree polynomial initially was fit through the volume- vs -pressure data for each cycle. This cycle-by-cycle analysis was done to investigate the possibility of hysteresis in the elastomer samples. The term hysteresis, in this sense, implies the sample would not return to its original volume after pressure cycling. This hysteresis was not observed in the sample of butyl-252. The type-W neoprene sample showed some slight evidence of the hysteresis phenomenon, but this could not be substantiated because mercury was driven into the thermistor when pressure was applied during the sample run with the neoprene sample. This small change in volume due to the mercury being driven into the thermistor was enough to account for the "volume shift" observed in the neoprene sample data. It was known that mercury was being driven into the thermistor because the thermistor inside the

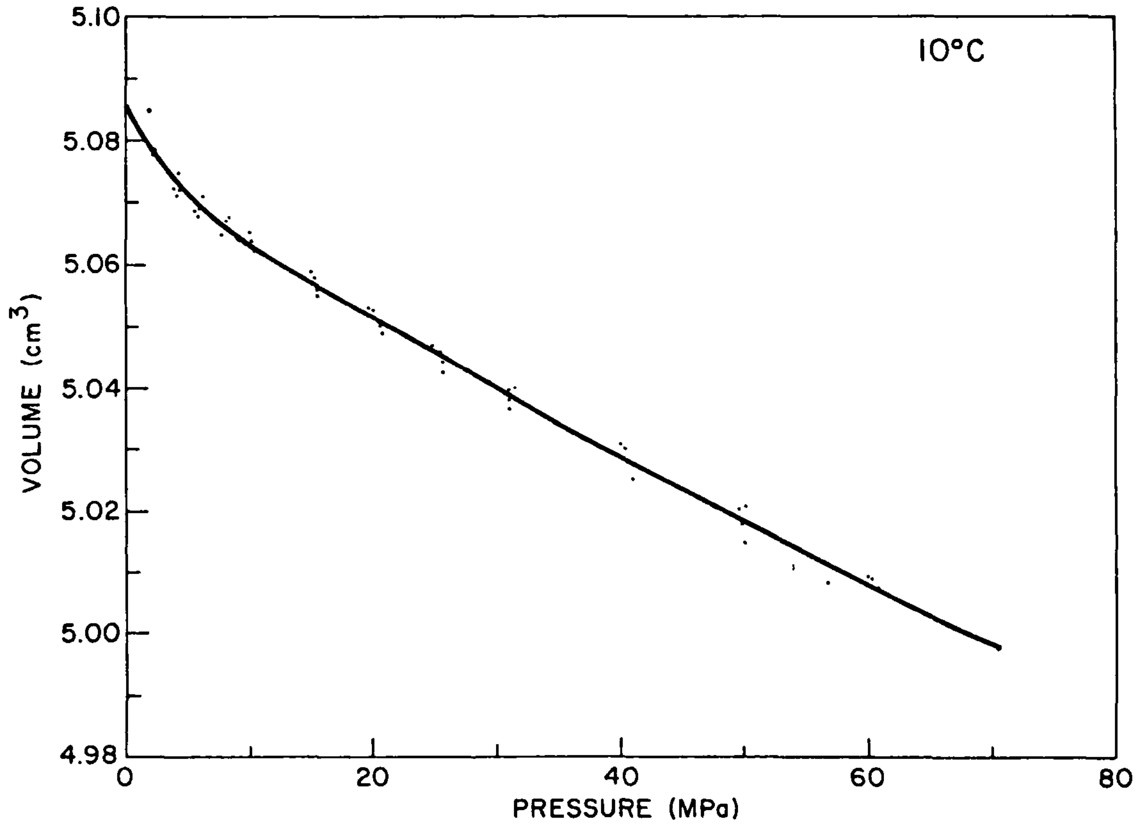


Fig. 10 — Pycnometer calibration run at 10°C. Volume (cm^3), shown on the ordinate, represents the volume of the mercury in the bore of the acoustic pycnometer. A sixth-degree polynomial is shown passing through the experimental points.

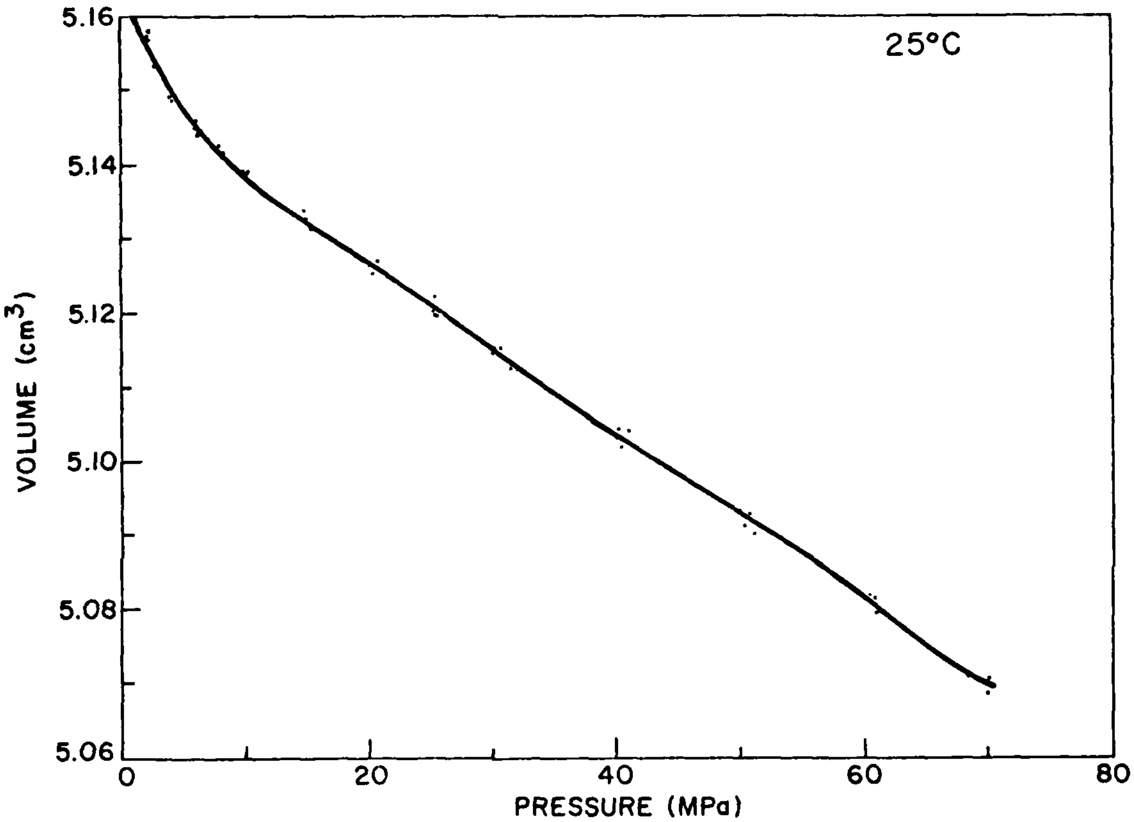


Fig. 11 — Pycnometer calibration run at 25°C. Volume (cm^3), shown on the ordinate, represents the volume of the mercury in the bore of the acoustic pycnometer. A sixth-degree polynomial is shown passing through the experimental points.

sample chamber short circuited during pressurization (i.e., exhibited zero resistance), and when the pressure was released, gave a temperature reading similar to the second thermistor on the outside of the pycnometer. Moreover, when the apparatus was disassembled, small droplets of mercury were actually found to be embedded in the epoxy encasing the thermistor. This behavior indicated that there was a flow of mercury into and out of the thermistor as the pressure was changed. The thermistor was modified so mercury could not short it out during the measurements on butyl-252.

The measured values of V_{BORE} made in the sample runs are given in Figs. 12, 14, and 17. These runs show no evidence of hysteresis, as stated earlier. In fact, it made no difference if all of the sample data were lumped together or analyzed cycle by cycle. A curve, in the form of a sixth-degree polynomial, was fitted to the lumped data points.

Figures 13, 15, and 18 show the actual sample volumes V_{SAMPLE} as a function of pressure at constant temperature for butyl-252 and type-W neoprene. Figure 15 is a plot of the volume of butyl-252 at 25°C as a function of pressure. This plot is of particular interest because it can give an idea of the accuracy of the volume determination when using the acoustic pycnometer. Theoretically, this zero-pressure value of the volume should coincide with the value of the volume of the butyl-252 sample determined by Archimedes' principle. The two determinations do,

in fact, agree closely. The difference between the two zero-pressure volume values of the butyl-252 is on the order of 0.22 percent. Since the zero-pressure extrapolation of the curve fit and the volume determination by Archimedes' principle are in such close agreement, discarding data below 2 MPa appears to be justified. The analysis performed to determine V_{SAMPLE} for the butyl-252 sphere was also applied to the measurements made on the type-W neoprene sample at 25°C. The results are shown in Fig. 18. The difference between the zero-pressure extrapolation of the curve in Fig. 18 and the volume measurement of the type-W neoprene sample made by Archimedes' principle yields an error of only 0.30 percent.

Figure 13 illustrates the behavior of the volume of the butyl-252 sample at 10°C as a function of pressure. No direct comparison of the zero-pressure extrapolation of the curve fit in Fig. 13 to a measurement of volume by Archimedes' principle can be made. In determining the volume by Archimedes' principle, one requires the water to be approximately the same temperature as the surrounding air. If a temperature gradient occurs in the water, convection currents in the water will be initiated and a false weighing of the sample in the water will result. Therefore, unless the water temperature can be kept constant, Archimedes' principle will produce erroneous results. Unfortunately, no apparatus for determining volumes by weighing the samples at different temperatures was available. An estimate can be made to compare the zero-pressure volume extrapolation of the butyl-252 sample at 10°C in

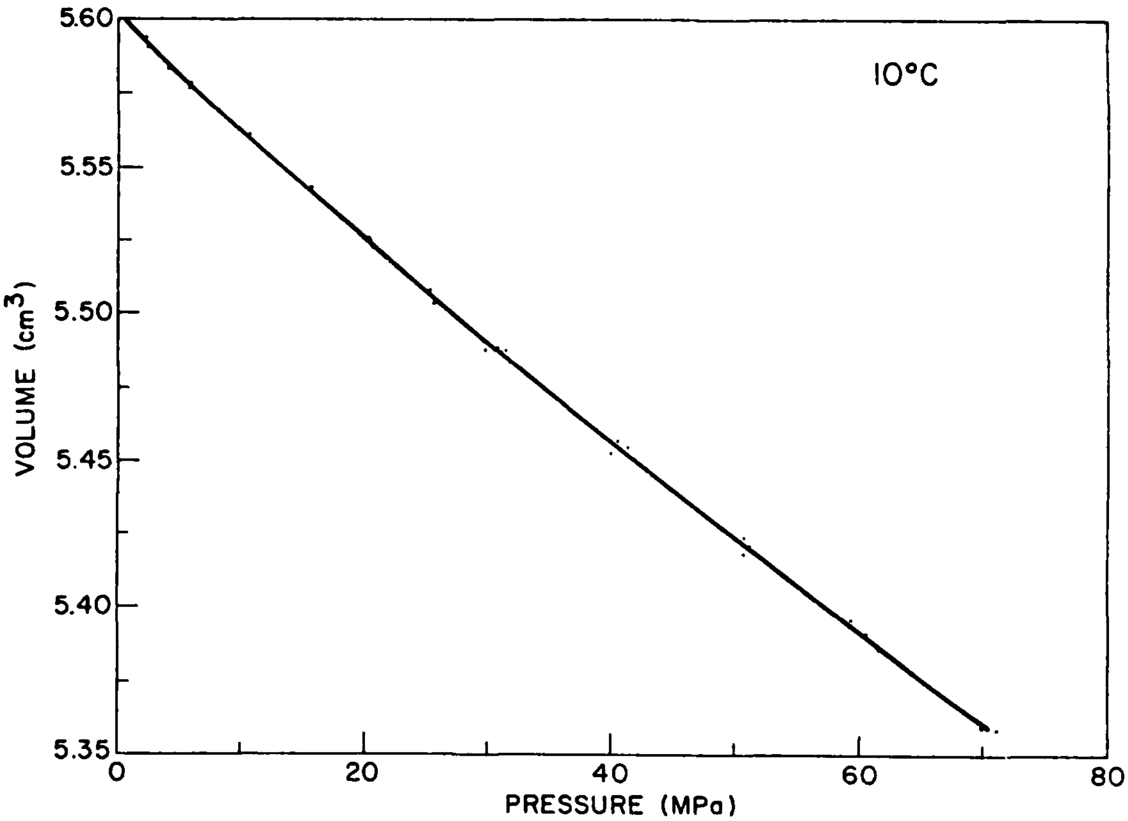


Fig. 12 — Pycnometer sample run of butyl-252 at 10°C. Volume (cm^3), shown on the ordinate, is the volume of the mercury in the bore of the acoustic pycnometer with a sample of butyl-252 present in the sample chamber. A sixth-degree polynomial is shown passing through the raw data.

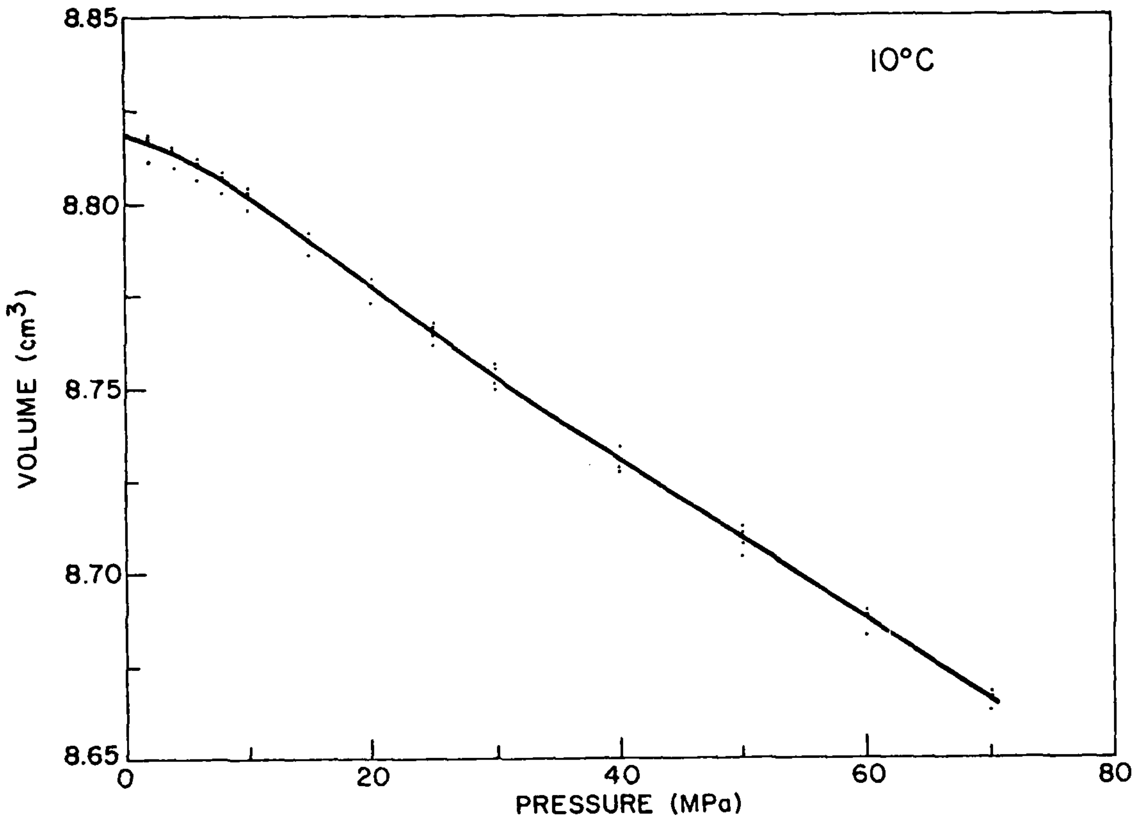


Fig. 13 — Volume of the butyl-252 sample at 10°C. Actual sample volume is given as a function of pressure. A sixth-degree polynomial is shown passing through the points calculated from Eq. (11b).

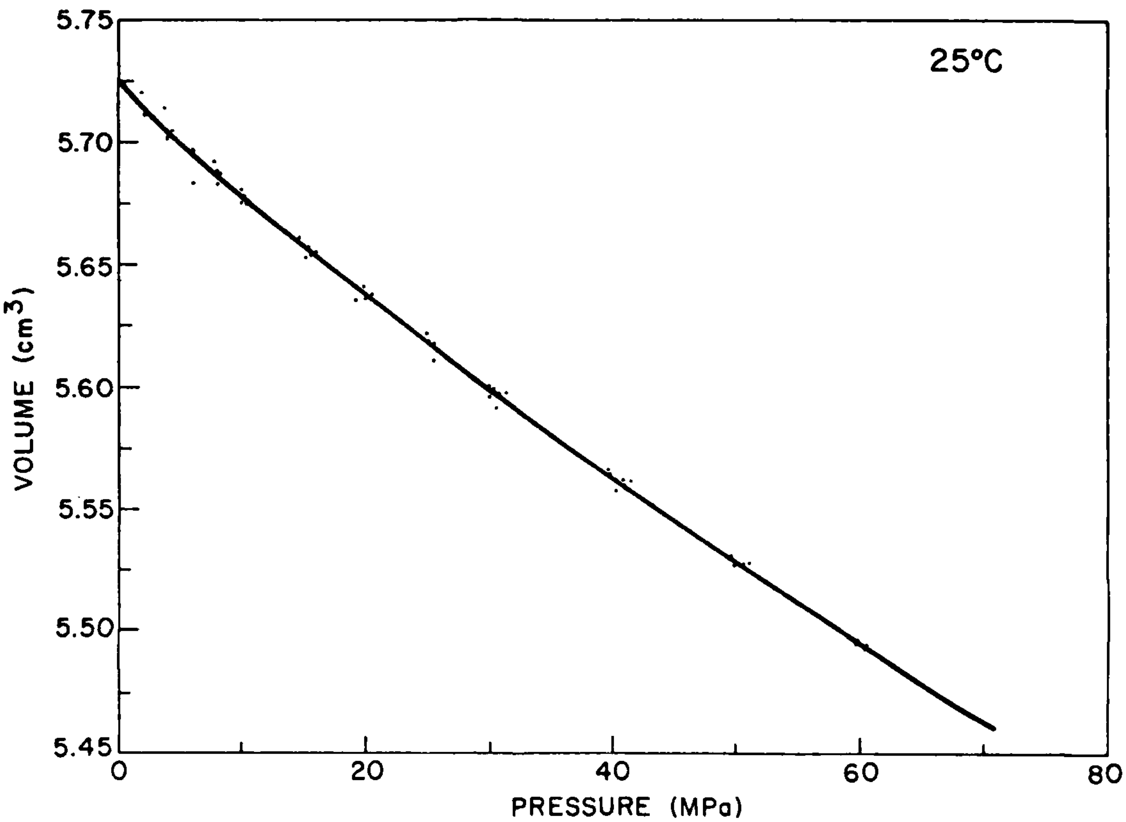


Fig. 14 — Pycnometer sample run of butyl-252 at 25°C. Volume (cm^3), shown on the ordinate is the volume of the mercury in the bore of the acoustic pycnometer with a sample of butyl-252 present in the sample chamber. A sixth-degree polynomial is shown passing through the raw data.

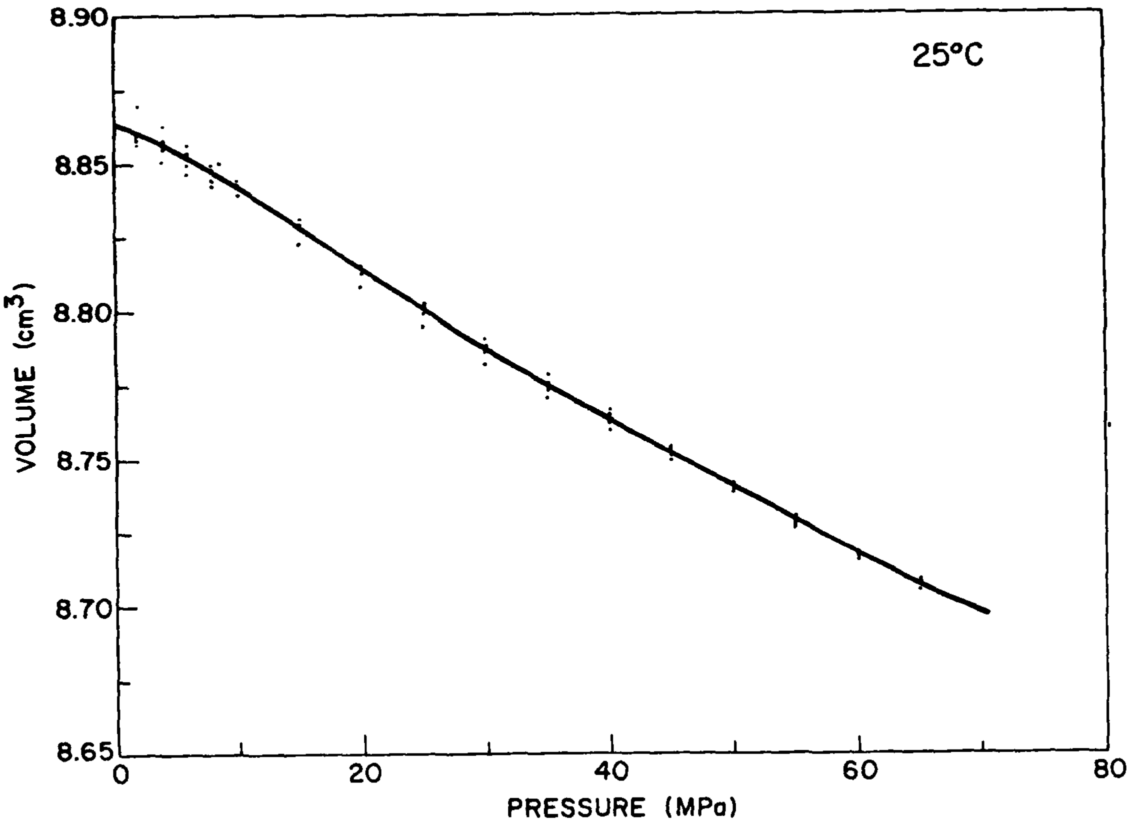


Fig. 15 — Volume of the butyl-252 sample of 25°C. Actual sample volume is given as a function of pressure. A sixth-degree polynomial is shown passing through the points calculated from Eq. (11b).

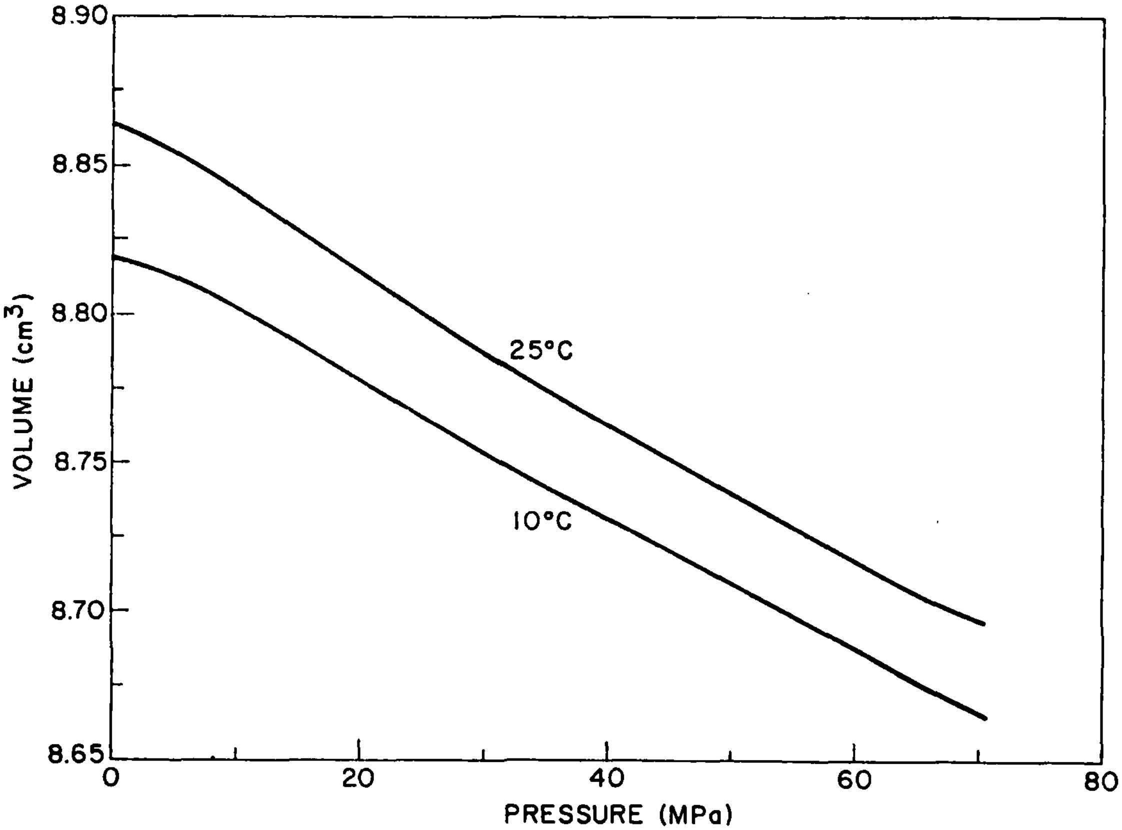


Fig. 16 — A comparison of results for butyl-252 at 10° C and 25° C

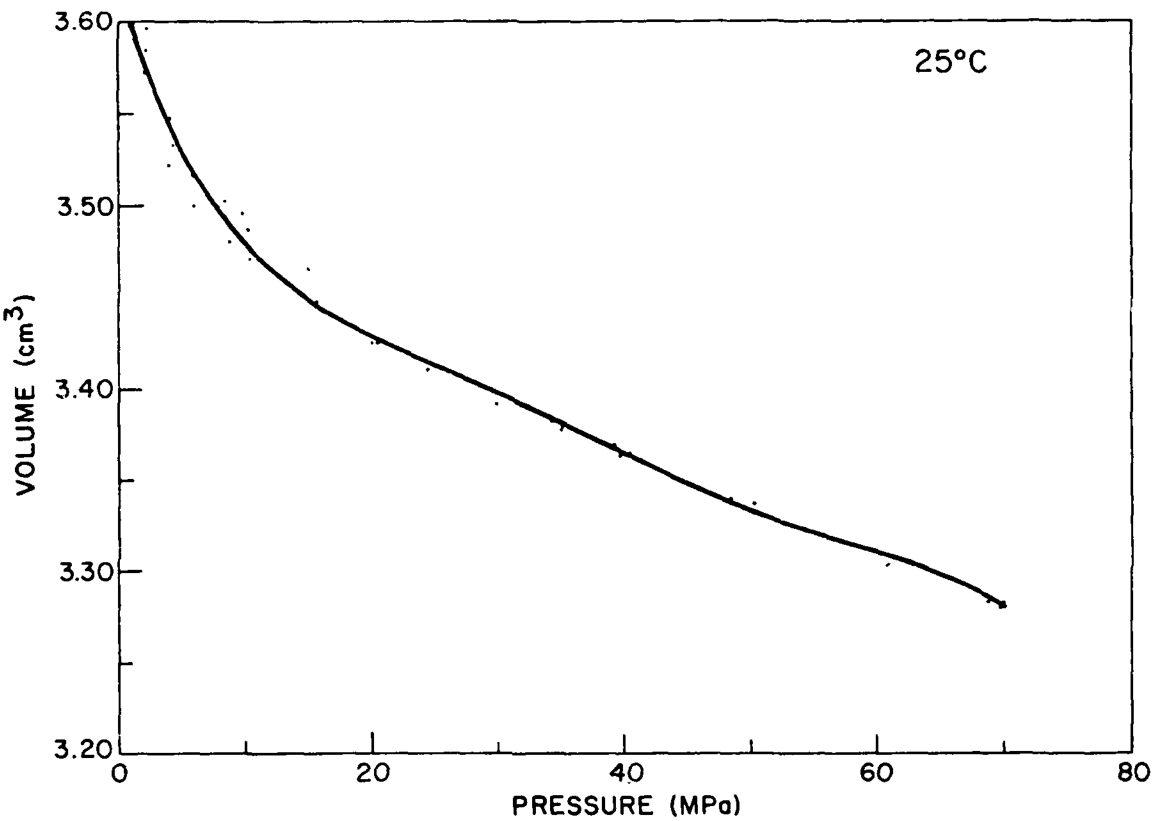


Fig. 17 — Pycnometer sample run of type-W neoprene at 25°C. Volume (cm^3), shown on the ordinate, is the volume of the mercury in the bore of the acoustic pycnometer with a sample of type-W neoprene present in the sample chamber. A sixth-degree polynomial is shown passing through the raw data.

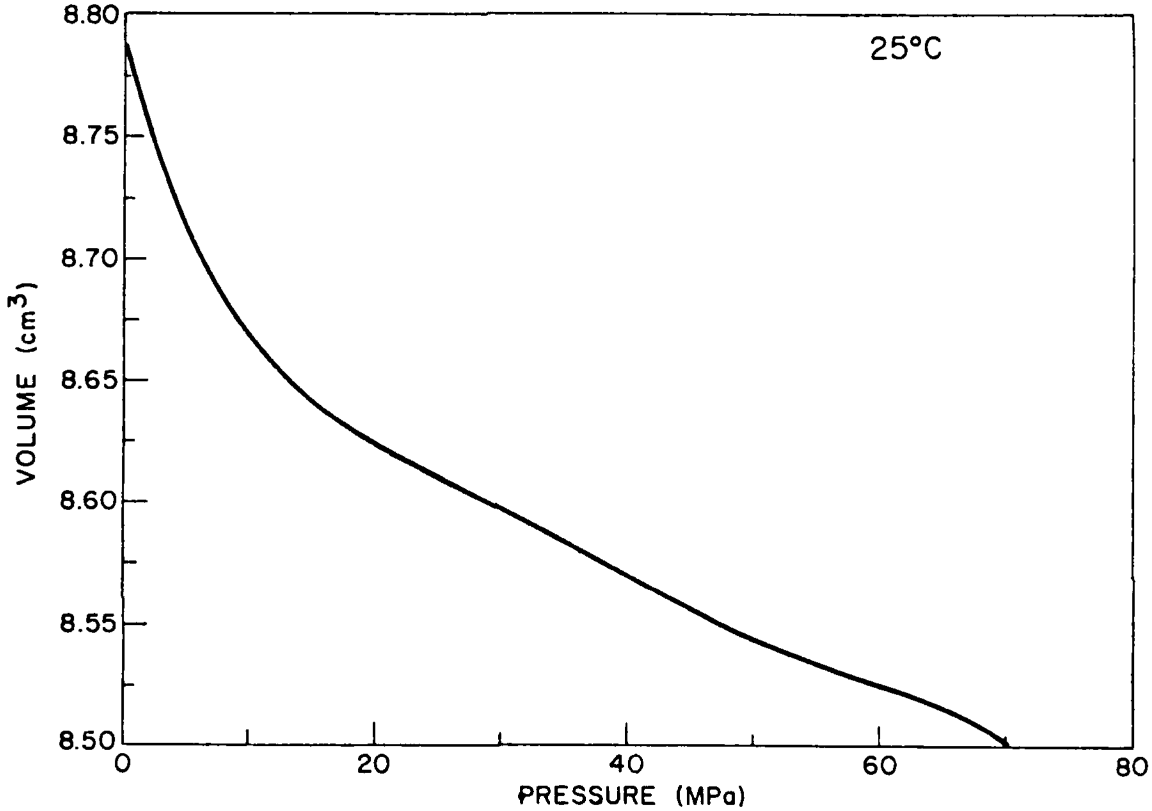


Fig. 18 — Volume of the type-W neoprene sample at 25° C. Actual sample volume is given as a function of pressure. A sixth-degree polynomial is shown.

Fig. 13 with an independently determined value of the volume of the sample by using the value of the butyl-252 sample at 25°C measured by Archimedes' principle and the volume coefficient of expansion for butyl rubber [9]. The value used for the coefficient of thermal expansion is $57 \times 10^{-5}/°C$. Performing this analysis, one calculates a value of 0.1 percent for the difference between the zero-pressure extrapolation of the curve fit in Fig. 13 and the volume calculated using the volume coefficient of thermal expansion for butyl rubber.

Figure 16 shows a comparison between the volume of the butyl-252 sample at 10°C and 25°C. At low pressures (less than 5 MPa), the plot of the measurement made on butyl-252 at 10°C does not exhibit the same amount of curvature. This might be attributed to a different compliance of the rubber at the lower temperature.

To obtain an idea of the actual precision of the acoustic pycnometer measurement technique, the observed deviation is compared to the random deviation computed by the error analysis in Appendix B. The precision of the experiment is quite good, as is seen in the graphs. The least-squares curves pass directly through the clusters of data points. The worst case of deviation is observed in Fig. 15, the plot for the sample volume of butyl-252 at 25°C. However, even at 2 MPa, the worst case, the observed deviation is only 0.17 percent. The maximum observed deviation for the plot of the sample volume of butyl-252 at 10°C in

Fig. 12 is 0.09 percent. The calculated random deviation when the error analysis was performed is on the order of 0.1 percent.

The results obtained for the type-W neoprene sample are not presented with the same degree of confidence as the results for the butyl-252 sample. As has been mentioned, mercury apparently flowed into and out of the thermistor located inside the sample chamber of the acoustic pycnometer when pressure was applied and released. Since the temperature could not be monitored as accurately because only the thermistor on the outside of the pycnometer was functioning, thermal equilibrium was not assured. Mercury intrusion into the thermistor in the sample chamber also meant that a small amount of mercury was being lost from the pycnometer into the thermistor inside the sample chamber, so the volume change of mercury in the bore was not due just to the volume change in the sample. This thermistor problem is also the reason why no data were obtained on the type-W neoprene sample at 10°C and occasioned the design of the thermistor plug.

The sixth-degree-polynomial least-squares coefficients for the volumes of the samples of butyl-252 and type-W neoprene at 25°C are respectively given in Tables I and II. The sixth-degree-polynomial coefficients for the volume of the butyl-252 sample at 10°C are also presented in Table I.

From the experimental results, the isothermal bulk modulus (see Appendix H) can be calculated by Eq. (H3). The results of the bulk-

Table I — Least-squares coefficients used for the calculation of the volume of the butyl-252 sample at 10°C and 25°C. The equation for the volume of the sample has the form: $V_S(P) = A_1 + A_2P + A_3P^2 + A_4P^3 + A_5P^4 + A_6P^5 + A_7P^6$.

Butyl-252 Least-Squares Coefficients, P = Ambient to 70 MPa				
	T = 10°C		T = 25°C	
A_1	+	0.881761×10^{1}	+	0.886270×10^{1}
A_2	-	0.439446×10^{-3}	-	0.106370×10^{-2}
A_3	-	0.175415×10^{-3}	-	0.157199×10^{-3}
A_4	+	0.718107×10^{-5}	+	0.633567×10^{-5}
A_5	-	0.147986×10^{-6}	-	0.119845×10^{-6}
A_6	+	0.152569×10^{-8}	+	0.108048×10^{-8}
A_7	-	0.625368×10^{-11}	-	0.367876×10^{-11}

Table II — Least-squares coefficients used for the calculation of the volume of the type-W neoprene sample at 25°C.

Type-W Neoprene Coefficients P = Ambient to 70 MPa, T = 25°C		
A_1	+	0.8803583×10^{1}
A_2	-	0.1917722×10^{-1}
A_3	+	0.8394465×10^{-3}
A_4	-	0.1701149×10^{-4}
A_5	+	0.7423981×10^{-7}
A_6	+	0.1733432×10^{-8}
A_7	-	$0.1609281 \times 10^{-10}$

modulus calculation are given in Fig. H1. As shown in Fig. H1, the isothermal bulk modulus of the butyl-252 sample rapidly decreases upon initial compression and then becomes relatively constant at pressures greater than 10 MPa. The bulk-moduli curves of the butyl-252 sample intersect at high pressure (~65 MPa). This is probably a numerical artifact associated with taking the derivatives of the sample-volume curves in Fig. 16, which are needed for the calculation of the bulk modulus. The drastic change in the low-pressure (less than 10 MPa) bulk-moduli results in Fig. H1 might be due to some sort of rearrangement of the molecular structure of the butyl-252 elastomer sample on a microscopic scale. At this time, this conclusion is purely speculative. At pressures greater than 10 MPa, the bulk-modulus of butyl-252 increases slightly as a function of pressure, or the rubber becomes stiffer with increasing pressure [10]. This behavior is also shown in Fig. H1.

VI. SUMMARY AND CONCLUSIONS

The experimental results given in the preceding section demonstrate that the acoustic pycnometer is an instrument for precise determination of the volume of an elastomer sample as a function of pressure at any temperature.

The only measure presently available of the accuracy of the pycnometer results is obtained by comparing the zero-pressure extrapolation of the least-squares curve fit of the volume of the samples to the volume of the samples when measured by Archimedes' principle at 25°C.

Since this comparison yielded errors of 0.22 percent and 0.30 percent, respectively, for the samples of butyl-252 and type-W neoprene, it can be assumed the method used in this research is accurate as well as precise.

VII. ACKNOWLEDGEMENT

This report is a facsimile of a thesis submitted by Erik K. Holmstrom to the faculty of the Department of Oceanography and Ocean Engineering of the Florida Institute of Technology in Melbourne, Florida, in partial fulfillment of the requirements for the degree of Master of Science in Oceanography.

While the authors of this report owe thanks to a number of persons at Florida Institute of Technology and at the NRL Underwater Sound Reference Detachment, the contributions of several individuals deserve particular acknowledgement. First, discussions with Pieter S. Dubbelday, Professor of Physics and Oceanography at Florida Institute of Technology, during the course of this work were both stimulating and helpful. Second, timely and diligent help with the computer analyses by Clementina M. Ruggiero materially aided the research effort and made it possible to complete it on schedule. Third, the help given us by Andrew J. Stepen throughout the course of this research proved invaluable. Not only did Mr. Stepen's expert advice on a number of practical questions substantially speed the progress of our experiments, but his dexterity and efficiency in constructing certain critical parts of the experimental

equipment contributed significantly to the success of the work described in this report. Finally, the efforts by Gina Y. Marshall, whose expert typing produced a professional looking document from a very imperfect draft manuscript, are greatly appreciated.

APPENDIX A

PULSE-ECHO OVERLAP TECHNIQUE

The time-of-flight measurement described earlier is done by a method called the pulse-echo overlap technique [1]. This technique was originally designed to accurately measure the speed of sound in a material. One calculates the speed of sound in a material from measurements of the time it takes for an ultrasonic pulse to propagate through the material and from knowledge of the thickness of the material sample.

Instead of using the pulse-echo overlap technique to measure the unknown speed of sound in a sample of material by measuring the time of flight in the sample, it was used in this investigation to determine the height of a column of mercury (the sound speed in which is known) in the bore of the pycnometer by Eq. (8). In the pulse-echo overlap method (Fig. A1) the cw oscillator frequency is adjusted so that its period is exactly equal to the round-trip time in the sample [12]. A standard oscilloscope is used to observe the pulse-echo train shown in Fig. 5. The time difference between two consecutive echoes is the time it takes for a sound pulse to travel from the transducer in the base of the bore of the pycnometer through the mercury column, to reflect from the float, and to return to the transducer. The Matec 122-B dual decade-delay generator, shown in Fig. A1, uses strobe signals (displayed via the oscilloscope) to highlight the first and second echoes in the pulse-echo train. The

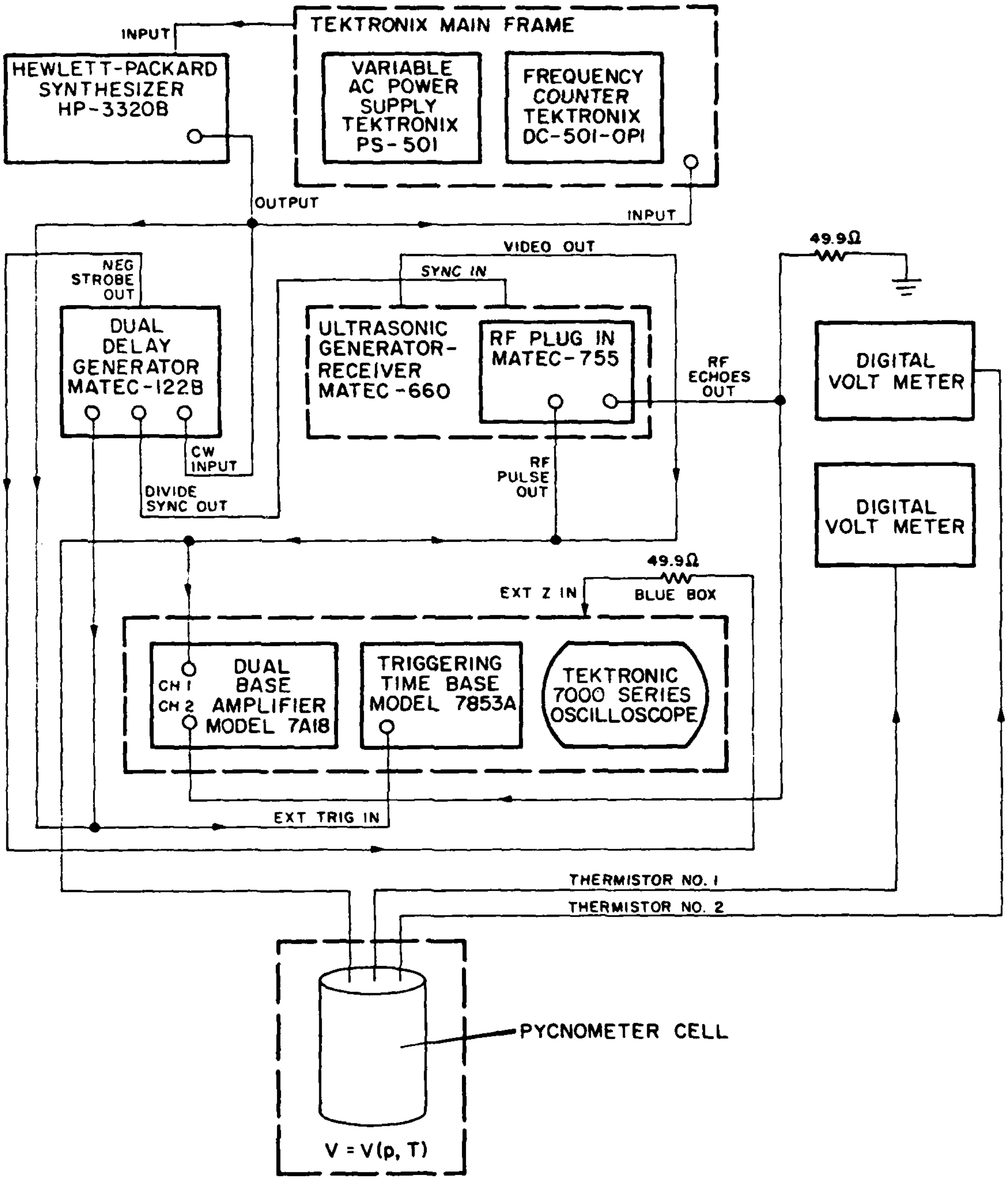


Fig. A1 — Schematic of acoustic-pycnometer measurement system

Hewlett-Packard frequency synthesizer is set approximately to the time difference between the first and second echoes as determined by a rough time measurement using the oscilloscope. These two echoes can be overlapped or superimposed when the horizontal sweep of the oscilloscope is triggered by the cw triggers in the Model 122-B (Sweep Sync Out-Direct). By carefully adjusting the vernier on the frequency synthesizer and by adjusting the time base on the oscilloscope, a precise overlap can be achieved (see Fig. A2); hence an accurate measurement is made of the time-of-flight in terms of a precisely set synthesizer frequency. When aligning the echoes on the oscilloscope, the earliest distinguishable feature is used as a reference to avoid mismatching the echoes. The only constraint is that the total sweep time must be less than the round-trip time in the mercury column to allow for retrace time in the oscilloscope [13].

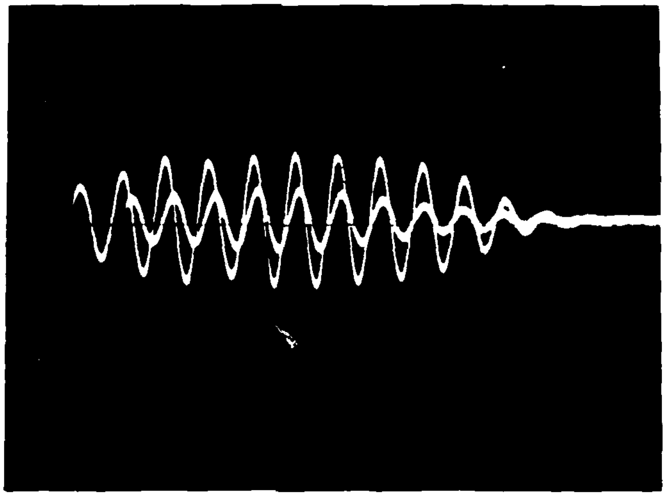


Fig. A2 — Pulse-echo overlap: timebase = 0.5 μs. The earliest arriving echo has the greatest amplitude.

APPENDIX B

ERROR ANALYSIS OF THE ACOUSTIC PYCNOMETER MEASUREMENT

The precision of the method used in the acoustic-pycnometer measurement can be investigated by examining the random deviation of the components of Eq. (14b). The maximum resultant effect due to several deviations in any measurement is simply the arithmetic sum of the individual deviations in the measurement [14], or

$$\Delta_{RES} = \Delta_1 + \Delta_2 + \ldots . + \Delta_j, \tag{B1}$$

where

Δ_{RES} = deviation of the resultant effect

Δ_1 through Δ_j = the deviations attributed to the various components of the measurement.

Each deviation in Eq. (B1) can be expressed as

$$\Delta_j = \left| \frac{\partial M}{\partial m_j} \delta_j \right| , \tag{B2}$$

where

M = the formula used to calculate the quantity desired and is a function of the properties measured

m_j = the property in which M exhibits a deviation

δ_j = the actual deviation in a particular property measured.

Equation (B1) represents a maximum possible random error because the sums of the individual deviations are taken to be positive quantities but in reality could have different signs. The most probable resultant deviation Δ_{RES}, according to method of least-squares [15], is

$$\Delta_{RES} = \sqrt{\Delta_1^{\,2} + \Delta_2^{\,2} + \Delta_3^{\,2} + \ldots\ldots + \Delta_n^{\,2}} \; . \tag{B3}$$

An expression for the resultant deviation of the calculation of the volume of the sample in the pycnometer measurement is obtained by applying Eq. (B1) to Eq. (14b). The resultant deviation is

$$\Delta V_{SAMPLE}(P,T) = \Delta V_{SAMPLE}(P_o,T_o) + \Delta V_{BORE} + \Delta V'_{BORE} + \Delta V(P,T). \tag{B4}$$

The individual deviations, in Eq. (B4), are in turn the sum of component deviations experienced when making their measurement. Therefore, the individual deviation of $V_{SAMPLE}(P_o,T_o)$ is

$$\Delta V_{SAMPLE}(P_o,T_o) = \left\{\Delta m_a\right\} + \left\{\Delta m_{H_2O}\right\} + \left\{\Delta \rho_{H_2O}\right\} , \tag{B5a}$$

where

$$\Delta V_{SAMPLE}(P_o,T_o) = V_{SAMPLE}(m_a,\ m_{H_2O},\ \rho_{H_2O}(P_o,T_o)).$$

The expression $\left\{\Delta m_a\right\}$ refers to the deviation in volume due to weighing the mass of the elastomer sample in air. The notation used

to express the deviation of the mass of the elastomer sample in air $\left\{\Delta m_a\right\}$ is

$$\left| \frac{\partial V_{SAMPLE}}{\partial m_a} \delta m_a \right| . \tag{B5b}$$

The individual deviation associated with measuring the volume of the mercury in the bore is

$$\Delta V_{BORE} = \left\{\Delta r_b\right\} + \left\{\Delta c\right\} + \left\{\Delta f\right\} , \tag{B6a}$$

since

$$V_{BORE} = V_{BORE}\ (r_b(P,T),\ c_{Hg}(P,T),\ f). \tag{B6b}$$

The expression for the individual deviation for the last term in Eq. (B4) is

$$\begin{aligned} \Delta V(P,T) = \left\{\Delta m'\right\} + \left\{\Delta m\right\} + \left\{\Delta \rho_{Hg}\right\} + \left\{\Delta V_{SAMPLE}(P_o,T_o)\right\} \\ + \left\{\Delta P_o\right\} + \left\{\Delta T_o\right\} + \left\{\Delta P\right\} + \left\{\Delta T\right\} , \end{aligned} \tag{B7}$$

where

$$V(P,T) = V(m',\ m,\ \rho_{Hg}(T_o),\ V_{SAMPLE}(P_oT_o),\ P_o,T_o,P,T).$$

The individual deviations given in Eqs. (B5a), (B6a), and (B7) can be analyzed by using Eq. (B2). Applying Eq. (B2) to Eq. (B5a), the deviation of the initial sample volume, one obtains

$$\Delta V_{SAMPLE}(P_o,T_o) = \left|\frac{\partial V_{SAMPLE}}{\partial m_a}\ \delta m_a\right| + \left|\frac{\partial V_{SAMPLE}}{\partial m_{H_2O}}\ \delta m_{H_2O}\right| + \left|\left(\frac{\partial V_{SAMPLE}}{\partial \rho_{H_2O}}\right)\left(\frac{\partial \rho_{H_2O}}{\partial T_o}\right)\delta T_o\right| . \tag{B8a}$$

After taking the appropriate derivatives, one finds that the equation for the random deviation for the initial sample volume is

$$\Delta V_{SAMPLE}(P_o,T_o) = \frac{1}{\rho_{H_2O}}\ \delta m_a + \frac{1}{\rho_{H_2O}}\ \delta m_{H_2O} + \left[\frac{(m_a + m_{H_2O})}{\rho^2_{H_2O}}\ \frac{\Delta\rho_{H_2O}}{\Delta T_o}\ \delta T_o\right] . \tag{B8b}$$

In Eq. (B8b), δm_a, δm_{H_2O}, and δT are observed deviations associated with measuring the mass of the sample in air, the mass of the sample in water, and the temperature, respectively. It should be noted that an appropriate estimate is needed for $\Delta\rho_{H_2O}/\Delta T$. This estimate is obtained by using the table of the density of water ρ_{H_2O} as a function of temperature and taking a finite difference for $\Delta\rho_{H_2O}$ between a temperature above and below the temperature T_o.

By the preceding analysis, the random deviations can be calculated for the case of the volumes of mercury in the bore ΔV_{BORE} and $\Delta V'_{BORE}$ and the volume of mercury associated with filling the pycnometer to a

different level V(P,T). Substituting this value obtained into Eq. (B4), one can obtain an estimate of the resultant deviation for the measurement of volume of any sample as function of pressure and temperature in the acoustic pycnometer.

It is found that the deviation calculated from Eq. (B4) is 0.0088 cm^3. This represents a random deviation in $V_{SAMPLE}(P,T)$ of 0.1 percent. This estimate of 0.1 percent is calculated from the following data:

$P = 0.0$ MPa	$\delta T = \pm 0.2°C$	$\delta m_a = \pm 0.0003$ g
$\delta P = \pm 0.1$ MPa	$T_o = 25°C$	$\delta m_{H_2O} = \pm 0.0003$ g
$P_o = 0.0$ MPa	$\delta T_o = \pm 0.2°C$	$r_b = 0.5545$ cm
$\delta P_o = \pm 0.1$ MPa	$f = 13.0$ kHz	$c_{Hg} = 147150$ cm/s
$T = 25°C$	$\delta f = \pm 5.0$ Hz	$\alpha_V = 3.6 \times 10^{-6}/°C$
		$\beta_V = 0.0/MPa$.

APPENDIX C

CALCULATION OF THE VOLUME OF MERCURY IN THE BORE OF THE ACOUSTIC PYCNOMETER

The volume of the mercury in the bore of the acoustic pycnometer is given by

$$V_{BORE} = AL \ , \tag{C1}$$

where

A = area of the bore

L = height of the mercury in the bore.

The area of the bore in Eq. (C1) is a function of temperature and pressure governed by the coefficient of thermal expansion and the coefficient of compressibility of the pycnometer container. The volume coefficient of thermal expansion is given by

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \ . \tag{C2}$$

Therefore, at constant pressure the change in volume per unit volume is,

$$\frac{dV}{V} = \alpha_V dT \ . \tag{C3}$$

The isothermal volume coefficient of compressibility is

$$\beta_V = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \ . \tag{C4}$$

Therefore, at constant temperature the change in volume per unit volume is

$$\frac{dV}{V} = - \beta_V dP \ . \tag{C5}$$

The expression for the change in area per unit area as a function of temperature and pressure would then take on the form

$$\frac{dA}{A} = \frac{2}{3}\left[\alpha_V dT - \beta_V dP\right] . \tag{C6}$$

Integrating Eq. (C6), one obtains

$$A(P,T) = \pi r_b^2 \exp[2(\alpha_V T - \beta_V P)/3]. \tag{C7}$$

The volume V_{BORE} of the mercury in the bore can be calculated by Eq. (C1) using Eq. (8) and Eq. (C7). It is found to be

$$V_{BORE}(P,T) = \frac{1}{2} c_{Hg}(P,T)\ t_f \pi r_b^2 \exp[2(\alpha_V T - \beta_V P)/3] \ . \tag{C8}$$

A Hewlett-Packard Model 9825 Calculator is used to calculate V_{BORE} from Eq. (C8). The program is shown on the following page.

```
0:  "start":fxd 5

1:  enp "Temp.
 [Celcius]",T

2:  enp "Pressure
 [MPa]",P

3:  enp "Freq.
 [kHz]",F

4:  1460→r6;.46→r
 7;.21→r8

5:  0→r9;9e-6→r10

6:  .5545→R

7:  (r6-r7*T+r8*
 P)*100→C

8:  prt "CHg [cm/
 s]",C

9:  .66667 (r9*T-
 r10*P)→D

10: exp(D)→E

11: .5*πR↑2*E*C/
 (F*1000)→B

12: prt "VHBG
 [ml] =",B;spc 2

13: gto 2
*1838
```

APPENDIX D

LEAST-SQUARES ANALYSIS AND COMPUTER PROGRAM

In order to use Eq. (14b) to determine the volume of an elastomer sample as a function temperature and pressure, it is necessary to determine an expression for the volume of the mercury in the bore of the pycnometer during the sample run and the calibration run. This can be accomplished by obtaining an equation of "best fit" to the experimental data by the method of least squares.

Since the experimental data did not follow a linear relation when plotted, a general least-squares solution is employed in the form of a rational fraction:

$$y(x) = \frac{A_1 + A_2x + A_3x^2 + A_4x^3 + A_5x^4 + A_6x^5 + A_7x^6}{A_8 + A_9x + A_{10}x^2 + A_{11}x^3 + A_{12}x^4 + A_{13}x^5 + A_{14}x^6} \quad \text{(D1)}$$

In Eq. (D1), the quantities x and y are the experimental observations. The coefficients A_1 through A_{14} are determined by the method of least squares as a best fit to the observed values of x and y. Rearranging Eq. (D1) into a more convenient form, one obtains

$$\begin{aligned} &A_8y + A_9xy + A_{10}x^2y + A_{11}x^3y + A_{12}x^4y + A_{13}x^5y + A_{14}x^6y \\ &- A_1 - A_2x - A_3x^2 - A_4x^3 - A_5x^4 - A_6x^5 - A_7x^6 = 0. \end{aligned} \quad \text{(D2)}$$

Equation (D2) represents an equation of best fit for a sixth-order rational fraction if no experimental errors are present in the observed quantities x and y. However, this is never the case, since all measurements are subject to error. Suppose one has n pairs of experimental measurements x_i, y_i ($i = 1, 2, \ldots n$). Then Eq. (D2) can be written in terms of the observed quantities x_i and y_i and the experimental error ν_i associated with measuring x_i and y_i

$$
\begin{aligned}
&A_8 y_1 + A_9 x_1 y_1 + A_{10} x_1^2 y_1 + \cdots - A_7 x_1^6 = \nu_1 \\
&A_8 y_2 + A_9 x_2 y_2 + A_{10} x_2^2 y_2 + \cdots - A_7 x_2^6 = \nu_2 \\
&A_8 y_i + A_9 x_i y_i + A_{10} x_i^2 y_i + \cdots - A_7 x_i^6 = \nu_i \\
&\quad\vdots \\
&A_8 y_n + A_9 x_n y_n + A_{10} x_n^2 y_n + \cdots - A_7 x_n^6 = \nu_n \,.
\end{aligned}
\tag{D3}
$$

In Eq. (D3), the subscripts associated with the quantities x_i, y_i, and ν_i refer to the i-th observation.

The least-squares principle states that the coefficients A_1 through A_{14}, in Eq. (D3), are the best fit to the data when the sum of the squares of the errors is a minimum [16], or

$$\frac{\partial}{\partial A_1}\left[\sum_{i=1}^{n} \nu_i^2\right] = 0$$

$$\frac{\partial}{\partial A_2}\left[\sum_{i=1}^{n} \nu_i^2\right] = 0$$

$$\frac{\partial}{\partial A_3}\left[\sum_{i=1}^{n} \nu_i^2\right] = 0 \tag{D4}$$

$$\vdots$$

$$\frac{\partial}{\partial A_{14}}\left[\sum_{i=1}^{n} \nu_i^2\right] = 0 \ .$$

After taking the derivatives in Eq. (D4), one obtains the final form for the equation

$$\sum_{i=1}^{n} \nu_n \frac{\partial \nu_n}{\partial A_1} = 0$$

$$\sum_{i=1}^{n} \nu_n \frac{\partial \nu_n}{\partial A_2} = 0$$

$$\sum_{i=1}^{n} \nu_n \frac{\partial \nu_n}{\partial A_3} = 0 \qquad \text{(D5)}$$

$$\vdots$$

$$\sum_{i=1}^{n} \nu_n \frac{\partial \nu_n}{\partial A_{14}} = 0.$$

Equation (D5) produces a system of linear simultaneous equations in terms of the observed quantities x_i, y_i. In order that this system of simultaneous equations is not linearly dependent, one of the coefficients must be set to a known value. To solve a system of simultaneous equations of this nature, in order to obtain the coefficients A_1 through A_{14}, a digital computer is needed. Equation (D5) can be written in matrix form as

$$[E]\ [A] = 0. \qquad \text{(D6)}$$

In Eq. (D6), the large matrix [E] represents the terms in Eq. (D5) after the appropriate derivatives have been taken and multiplied

by the error term ν. The [A] matrix is a column matrix that represents the coefficients which best fit the observed ata.

The computer program, RAGT.FTN, using NRL-USRD's PDP-11/45 computer, was written in FORTRAN to do the least-squares analysis. The program was written in a general fashion to try and accommodate various types of data. For instance, a polynomial curve fit is obtained by simply initializing the coefficient A_8 to 1 and by setting coefficients A_9 through A_{14} to zero. If a lower-degree polynomial fit is desired, one simply suppresses the appropriate coefficient by setting it to zero. The subroutine SELECT.FTN allows the user to select any coefficient for initialization. The subroutine SUPRES.FTN sets any desired coefficient to zero to lower the degree of polynomial. The subroutine DSIMEQ.FTN solves the system of simultaneous equations shown in Eq. (D6), by means of Gaussian elimination in double precision. Once the least-squares coefficients, represented by the column matrix [A] in Eq. (D6), are calculated, the subroutine YCALCU.FTN, uses these least-squares coefficients to recalculate the function y(x) in Eq. (D1). A listing of RAGT.FTN and all the subroutines used follows:

```
C              PROGRAM DIRECTORY
C         DATA TO BE ENTERED
C         M=# OF DATA POINTS
C         XPRESS(100)= ARRAY TO HOLD PRESSURE DATA
C         YVOL(100)= ARRAY TO HOLD VHGB DATA
C         A(14,14)= ARRAY TO HOLD VARIOUS SUMS
C         B(N)= COLUMN MATRIX
C         N= NUMBER OF SIMULTANEOUS EQUATIONS
          BYTE ANS(4)
          DIMENSION XPRESS(100),YVOL(100),XINC(100),YCALC(100)
          DOUBLE PRECISION A(14,14),B(14),X(14),VALUE(14),DX1,DX2,DX3,
          1DX4,DX5,DX6,DX7,DX8,DX9,DX10,DX11,DX12,DY1,DY2,DX1Y1,DX1Y2,
          1DX2Y1,DX2Y2,DX3Y1,DX3Y2,DX4Y1,DX4Y2,DX5Y1,DX5Y2,DX6Y1,DX6Y2,
          1DX7Y1,DX7Y2,DX8Y1,DX8Y2,DX9Y1,DX9Y2,DX10Y1,DX10Y2,DX11Y1,
          1DX11Y2,DX12Y1,DX12Y2,X1,X2,X3,X4,X5,X6,X7,X8,X9,X10,X11,X12,
          1Y1,Y2,X1Y1,X1Y2,X2Y1,X2Y2,X3Y1,X3Y2,X4Y1,X4Y2,X5Y1,X5Y2,
          1X6Y1,X6Y2,X7Y1,X7Y2,X8Y1,X8Y2,X9Y1,X9Y2,X10Y1,X10Y2,X11Y1,
          1X11Y2,X12Y1,X12Y2,DUM,SCALE
          WRITE(5,1000)
1000      FORMAT(/,'$USE OLD DATA?')
          READ(5,1010,END=800)ANS
1010      FORMAT(4A1)
          IF(ANS(1).EQ.'N')GO TO 870
          OPEN(UNIT=1,NAME=' RAGT.DAT',TYPE='OLD')
          READ(1,18)M
          DO 860 I=1,M
               READ(1,12)XPRESS(I),YVOL(I)
860       CONTINUE
          GO TO 110
870       OPEN(UNIT=1,NAME=' RAGT.DAT',TYPE='NEW')
C         ALLOCATE STORAGE
          DO 10 I=1,100
          XPRESS(I)=0.0
          YVOL(I)=0.0
10        CONTINUE
          WRITE(5,15)
 15       FORMAT(5X,' $ENTER THE NUMBER OF DATA POINTS')
          READ(5,18)M
 18       FORMAT(I10)
          DO 100 J=1,M
          WRITE(5,11)
 11       FORMAT(1X,' XPRESS,YVOL')
          READ(5,12)XPRESS(J),YVOL(J)
 12       FORMAT(2F10.0)
100       CONTINUE
          WRITE(1,18)M
          DO 40 I=1,M
               WRITE(1,1020)XPRESS(I),YVOL(I)
1020      FORMAT(F10.5,F10.5)
40        CONTINUE
110       CLOSE(UNIT=1)
          WRITE(5,1040)
1040      FORMAT(/,' $ENTER THE NUMBER OF SIMULTANEOUS EQUATIONS')
          READ(5,1050)N
1050      FORMAT(I4)
          DATA X1,X2,X3,X4,X5,X6,X7,X8,X9,X10,X11,X12,Y1,Y2,X1Y1,X1Y2,
          1X2Y1,X2Y2,X3Y1,X3Y2,X4Y1,X4Y2,X5Y1,X5Y2,X6Y1,X6Y2,X7Y1,
          1X7Y2,X8Y1,X8Y2,X9Y1,X9Y2,X10Y1,X10Y2,X11Y1,X11Y2,X12Y1,
          1X12Y2/38*0.0D+02/
          DO 50 I=1,M
C         SET UP DUMMY STORAGE
          DX1=DBLE(XPRESS(I))
          DX2=DX1*DX1
          DX3=DX1*DX2
```

```
      DX4=DX2*DX2
      DX5=DX2*DX3
      DX6=DX3*DX3
      DX7=DX1*DX6
      DX8=DX2*DX6
      DX9=DX3*DX6
      DX10=DX4*DX6
      DX11=DX5*DX6
      DX12=DX6*DX6
      DY1=DBLE(YVOL(I))
      DY2=DY1*DY1
      DX1Y1=DX1*DY1
      DX1Y2=DX1*DY2
      DX2Y1=DX2*DY1
      DX2Y2=DX2*DY2
      DX3Y1=DX3*DY1
      DX3Y2=DX3*DY2
      DX4Y1=DX4*DY1
      DX4Y2=DX4*DY2
      DX5Y1=DX5*DY1
      DX5Y2=DX5*DY2
      DX6Y1=DX6*DY1
      DX6Y2=DX6*DY2
      DX7Y1=DX7*DY1
      DX7Y2=DX7*DY2
      DX8Y1=DX8*DY1
      DX8Y2=DX8*DY2
      DX9Y1=DX9*DY1
      DX9Y2=DX9*DY2
      DX10Y1=DX10*DY1
      DX10Y2=DX10*DY2
      DX11Y1=DX11*DY1
      DX11Y2=DX11*DY2
      DX12Y1=DX12*DY1
      DX12Y2=DX12*DY2
C     START ACCUMULATING SUMS
      X1=X1+DX1
      X2=X2+DX2
      X3=X3+DX3
      X4=X4+DX4
      X5=X5+DX5
      X6=X6+DX6
      X7=X7+DX7
      X8=X8+DX8
      X9=X9+DX9
      X10=X10+DX10
      X11=X11+DX11
      X12=X12+DX12
      Y1=Y1+DY1
      Y2=Y2+DY2
      X1Y1=X1Y1+DX1Y1
      X1Y2=X1Y2+DX1Y2
      X2Y1=X2Y1+DX2Y1
      X2Y2=X2Y2+DX2Y2
      X3Y1=X3Y1+DX3Y1
      X3Y2=X3Y2+DX3Y2
      X4Y1=X4Y1+DX4Y1
      X4Y2=X4Y2+DX4Y2
      X5Y1=X5Y1+DX5Y1
      X5Y2=X5Y2+DX5Y2
      X6Y1=X6Y1+DX6Y1
      X6Y2=X6Y2+DX6Y2
      X7Y1=X7Y1+DX7Y1
      X7Y2=X7Y2+DX7Y2
```

```
      X8Y1=X8Y1+DX8Y1
      X8Y2=X8Y2+DX8Y2
      X9Y1=X9Y1+DX9Y1
      X9Y2=X9Y2+DX9Y2
      X10Y1=X10Y1+DX10Y1
      X10Y2=X10Y2+DX10Y2
      X11Y1=X11Y1+DX11Y1
      X11Y2=X11Y2+DX11Y2
      X12Y1=X12Y1+DX12Y1
      X12Y2=X12Y2+DX12Y2
50    CONTINUE
C     STORE SUMS IN MATRICES A(N,N) AND B(N)
      A(1,1)=Y2
      A(2,1)=X1Y2
      A(2,2)=X2Y2
      A(3,1)=X2Y2
      A(3,2)=X3Y2
      A(3,3)=X4Y2
      A(4,1)=X3Y2
      A(4,2)=X4Y2
      A(4,3)=X5Y2
      A(4,4)=X6Y2
      A(5,1)=X4Y2
      A(5,2)=X5Y2
      A(5,3)=X6Y2
      A(5,4)=X7Y2
      A(5,5)=X8Y2
      A(6,1)=X5Y2
      A(6,2)=X6Y2
      A(6,3)=X7Y2
      A(6,4)=X8Y2
      A(6,5)=X9Y2
      A(6,6)=X10Y2
      A(7,1)=X6Y2
      A(7,2)=X7Y2
      A(7,3)=X8Y2
      A(7,4)=X9Y2
      A(7,5)=X10Y2
      A(7,6)=X11Y2
      A(7,7)=X12Y2
      A(8,1)=-Y1
      A(8,2)=-X1Y1
      A(8,3)=-X2Y1
      A(8,4)=-X3Y1
      A(8,5)=-X4Y1
      A(8,6)=-X5Y1
      A(8,7)=-X6Y1
      A(8,8)=N
      A(9,1)=-X1Y1
      A(9,2)=-X2Y1
      A(9,3)=-X3Y1
      A(9,4)=-X4Y1
      A(9,5)=-X5Y1
      A(9,6)=-X6Y1
      A(9,7)=-X7Y1
      A(9,8)=X1
      A(9,9)=X2
      A(10,1)=-X2Y1
      A(10,2)=-X3Y1
      A(10,3)=-X4Y1
      A(10,4)=-X5Y1
      A(10,5)=-X6Y1
      A(10,6)=-X7Y1
      A(10,7)=-X8Y1
```

```
      A(10,8)=X2
      A(10,9)=X3
      A(10,10)=X4
      A(11,1)=-X3Y1
      A(11,2)=-X4Y1
      A(11,3)=-X5Y1
      A(11,4)=-X6Y1
      A(11,5)=-X7Y1
      A(11,6)=-X8Y1
      A(11,7)=-X9Y1
      A(11,8)=X3
      A(11,9)=X4
      A(11,10)=X5
      A(11,11)=X6
      A(12,1)=-X4Y1
      A(12,2)=-X5Y1
      A(12,3)=-X6Y1
      A(12,4)=-X7Y1
      A(12,5)=-X8Y1
      A(12,6)=-X9Y1
      A(12,7)=-X10Y1
      A(12,8)=X4
      A(12,9)=X5
      A(12,10)=X6
      A(12,11)=X7
      A(12,12)=X8
      A(13,1)=-X5Y1
      A(13,2)=-X6Y1
      A(13,3)=-X7Y1
      A(13,4)=-X8Y1
      A(13,5)=-X9Y1
      A(13,6)=-X10Y1
      A(13,7)=-X11Y1
      A(13,8)=X5
      A(13,9)=X6
      A(13,10)=X7
      A(13,11)=X8
      A(13,12)=X9
      A(13,13)=X10
      A(14,1)=-X6Y1
      A(14,2)=-X7Y1
      A(14,3)=-X8Y1
      A(14,4)=-X9Y1
      A(14,5)=-X10Y1
      A(14,6)=-X11Y1
      A(14,7)=-X12Y1
      A(14,8)=X6
      A(14,9)=X7
      A(14,10)=X8
      A(14,11)=X9
      A(14,12)=X10
      A(14,13)=X11
      A(14,14)=X12
C     DUE TO THE SYMMETRY OF MATRIX A(N,N), THE REMAINDER OF THE
C     MATRIX CAN STORED BY THE USE OF A LOOP USING
C     THE RELATION A(K,J)=A(J,K)
      DO 120 K=2,N
      KK=K-1
      DO 115 J=1,KK
              A(J,K)=A(K,J)
115   CONTINUE
120   CONTINUE
C     CHOOSE THE SCALING FACTOR
      [illegible]
```

```
1220    FORMAT(/,' $ENTER THE SCALING FACTOR')
        READ(5,1230)SCALE
1230    FORMAT(D24.17)
C       SCALE THE MATRIX A(N,N)
        DUM=(0.1000D+01)/SCALE
        DO 75 J=1,N
        DO 70 K=1,N
                A(J,K)=A(J,K)*DUM
 70     CONTINUE
 75     CONTINUE
C       THE SUBROUTINE SELECT ALLOWS YOU TO SELECT ANY OF THE CO-
C       EFFICIENTS  FOR INITIALIZATION
        CALL SELECT(N,A,B,VALUE)
        WRITE(5,1200)
1200    FORMAT(/,' $SUPPRESS ANY COEFFICIENT?')
        READ(5,1010,END=800)ANS
        IF(ANS(1).EQ.'N')GO TO 1300
        CALL SUPRES(N,A,B,X)
D       WRITE(5,1060)
D1060   FORMAT(' READY TO CALL DSIMEQ')
C       CALL SUBROUTINE TO SOLVE SIMULTANEOUS EQ.
1300    CALL DSIMEQ(N,A,B,X)
C       CALL SUBROUTINE YCAL TO CALCULATE VALUES OF YVOL
        CALL YCAL(N,X,YCALC,XINC)
800     WRITE(5,2000)
2000    FORMAT(' PROGRAM EXITS!')
        GO TO 900
900     CALL EXIT
        END
```

```
      SUBROUTINE DSIMEQ(N,A,B,X)
      DOUBLE PRECISION A(14,14),B(14),X(14),DET,SUM,C
      DIMENSION JPRM(14)
D     WRITE(5,50)
D50   FORMAT(' ENTERED SUBROUTINE')
      DET=1.0D 00
      DO 13 I=1,N
      X(I)=0.0D 00
13    JPRM(I)=I
C     FIND THE ELEMENT OF MAXIMUM ABSOLUTE VALUE
      DO 1 K=1,N
      C=A(K,K)
      II=K
      JJ=K
      DO 2 J=K,N
      DO 2 I=K,N
      IF (DABS(C)-DABS(A(I,J)))3,2,2
 3    C=A(I,J)
      II=I
      JJ=J
 2    CONTINUE
      DET=DET*C
D     WRITE(5,55)DET
D55   FORMAT(5X,' DET='D24.17)
      IF(DABS(DET))20,20,30
20    WRITE(5,100)
100   FORMAT(' MATRIX A(N,N)IS SINGULAR')
      CALL EXIT
30    B(II)=B(II)/C
C     DIVIDE EACH ELEMENT OF THE IITH ROW BY C
      KPO=K+1
      DO 4 J=K,N
 4    A(II,J)=A(II,J)/C
      A(II,JJ)=1.0D 00
      IF (II.EQ.K)GO TO 60
C     SWITCH THE KTH ROW AND THE IITH ROW
      DO 5 J=K,N
      C=A(K,J)
      A(K,J)=A(II,J)
 5    A(II,J)=C
      C=B(K)
      B(K)=B(II)
      B(II)=C
 60   IF (JJ.EQ.K)GO TO 70
C     STORE THE LOCATION OF THE MAX PIVOT
      II=JPRM(JJ)
      JPRM(JJ)=JPRM(K)
      JPRM(K)=II
C     SWITCH THE KTH AND THE JJTH COLUMNS
      DO 6 I=1,N
      C=A(I,K)
      A(I,K)=A(I,JJ)
 6    A(I,JJ)=C
C     GET SUB COLUMN OF ZEROES IN THE KTH COLUMN
70    IF(K.EQ.N)GO TO 1
      DO 7 I=KPO,N
      DO 8 J=KPO,N
 8    A(I,J)=A(I,J)-A(I,K)*A(K,J)
      B(I)=B(I)-A(I,K)*B(K)
 7    A(I,K)=0.0D 00
 1    CONTINUE
C     OBTAIN THE X'S BY BACK SUBSTITUTION
      DO 9 I=1,N
      K=N-I+1
```

```
        KPO=K+1
        SUM=0.0D 00
        IF(KPO-N)24,24,26
24      DO 10 J=KPO,N
        SUM=SUM+X(J)*A(K,J)
10      CONTINUE
26      X(K)=B(K)-SUM
 9      CONTINUE
C       ORDER THE X'S
        DO 11 I=1,N
11      B(I)=X(I)
        DO 12 I=1,N
        II=JPRM(I)
        X(II)=B(I)
12      CONTINUE
C       WRITE OUT THE VALUES OF X(N)
        DO 101 J=1,N
                WRITE(5,99)J,X(J)
 99             FORMAT(/,5X,' X(',I2,')=',D24.17)
101     CONTINUE
        RETURN
        END
```

```
      SUBROUTINE SELECT(N,A,B,VALUE)
C     SET UP CATELOG ARRAY ICAT(N)
      DIMENSION ICAT(14)
      DOUBLE PRECISION A(14,14),B(14),VALUE(14)
C     INITIALIZE B(N),ICAT(N),AND VALUE (N)
      DO 10 J=1,N
            B(J)=0.0D+00
            ICAT(J)=1
            VALUE(J)=0.0D+00
 10   CONTINUE
C     SELECT THE COEFFIECIENTS TO BE INITIALIZED
      WRITE(5,20)
20    FORMAT(/,' HOW MANY COEFFICIENTS TO BE INITIALIZED?')
      READ(5,30)NN
 30   FORMAT(I2)
      DO 60 I=1,NN
            WRITE(5,40)
 40         FORMAT(/,' WHICH COEFFICIENTS TO BE INITIALIZED?')
            READ(5,50)II
 50         FORMAT(I2)
            ICAT(II)=0
            WRITE(5,55)
 55         FORMAT(/,' WHAT VALUE DO YOU WANT COEFFICIENTS TO BE?')
            READ(5,58)VALUE(II)
 58         FORMAT(D24.17)
 60   CONTINUE
C     IN ORDER FOR THE SET OF EQUATIONS TO BE INDEPENDENT INSERT
C     THE APPROPRIATE VALUES IN B(N) AND A(N,N).
      DO 80 J=1,N
      DO 70 K=1,N
      IF(ICAT(K).NE.0)GO TO 70
            A(K,J)=0.0D+00
            A(K,K)=1.0D+00
            B(K)=VALUE(K)
 70   CONTINUE
 80   CONTINUE
      DO 90 J=1,N
      WRITE(5,1040)J,B(J)
1040  FORMAT(/,' B(',I2,')=',D24.17)
 90   CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SUPRES(N,A,B,X)
C     SET UP CATELOG ARRAY JCAT(N)
      DIMENSION JCAT(14)
      DOUBLE PRECISION A(14,14),B(14),X(14)
C     INITIALIZE JCAT(N) TO ONE
      DO 20 J=1,N
              JCAT(J)=1
   20 CONTINUE
      WRITE(5,40)
   40 FORMAT(/,' HOW MANY VALUES OF JCAT=0')
      READ(5,60)KK
   60 FORMAT(I2)
      DO 80 L=1,KK
              WRITE(5,90)
   90         FORMAT(/,' WHICH VALUES OF JCAT=0')
              READ(5,95)I
   95         FORMAT(I2)
              JCAT(I)=0
   80 CONTINUE
C     SET THE ROW IN MATRIX A(N,N) = 0
      DO 300 J=1,N
      DO 200 K=1,N
              IF(JCAT(K).NE.0)GO TO 200
  150         A(K,J)=0.0D+00
              A(K,K)=1.0D+00
              B(K)=0.0D+00
D     WRITE(5,100)K,J,A(K,J)
D100  FORMAT(/' A(',I2,' ,',I2,' )=',D24.17)
200   CONTINUE
300   CONTINUE
      RETURN
      END
```

```
        SUBROUTINE YCALCU(N,X,YCALC,XINC)
        DOUBLE PRECISION X(14)
        DIMENSION XINC(500),YCALC(500),XSING(14),X(1),Y(1)
        DATA DEN1,DEN2,DEN3,DEN4,DEN5,DEN6,XNUM1,XNUM2,XNUM3,XNUM4,
        1XNUM5,XNUM6/12*0.0/
        BYTE FILEX(32)
D       WRITE(5,1095)
D1095   FORMAT(' ENTERED SUBROUTINE YCAL')
C       PUT X(N) INTO SINGLE PRECISION
        DO 20 L=1,N
                XSING(L)=SNGL(X(L))
D       WRITE(5,1100)XSING(L)
D1100   FORMAT(/' XSING=',E15.5)
20      CONTINUE
        WRITE(5,21)
 21     FORMAT(/,' MAXIMUM X YOU WISH TO GO')
        READ(5,24)IX
 24     FORMAT(I4)
        J=IX+1
        WRITE(5,31)
 31     FORMAT(/,'  X INCREMENT VALUE?')
        READ(5,35)XINCRE
 35     FORMAT(F10.0)
C       ALLOCATE STORAGE
        DO 30 I=1,J
                XINC(I)=0.0
                YCALC(I)=0.0
30      CONTINUE
D       WRITE(5,1125)
D1125   FORMAT(' HAVE SET UP STORAGE')
C       SET UP LOOP TO CALCULATE YCALC(K)
                DXINC=0.0
        DO 50 K=1,J
                XINC(K)=DXINC
                DXINC2=DXINC*DXINC
                DXINC3=DXINC2*DXINC
                DXINC4=DXINC2*DXINC2
                DXINC5=DXINC2*DXINC3
                DXINC6=DXINC3*DXINC3
                DEN1=XSING(2)*DXINC
                DEN2=XSING(3)*DXINC2
                DEN3=XSING(4)*DXINC3
                DEN4=XSING(5)*DXINC4
                DEN5=XSING(6)*DXINC5
                DEN6=XSING(7)*DXINC6
                XNUM1=XSING(9)*DXINC
                XNUM2=XSING(10)*DXINC2
                XNUM3=XSING(11)*DXINC3
                XNUM4=XSING(12)*DXINC4
                XNUM5=XSING(13)*DXINC5
                XNUM6=XSING(14)*DXINC6
C       FORM NUMERATOR AND DENOMINATOR OF YCALC
                XNUM=XSING(8)+XNUM1+XNUM2+XNUM3+XNUM4+XNUM5+XNUM6
                XDEN=XSING(1)+DEN1+DEN2+DEN3+DEN4+DEN5+DEN6
C       CALCULATE YCALC
                YCALC(K)=XNUM/XDEN
C       INCREMENT DXINC
                DXINC=DXINC+XINCRE
50      CONTINUE
        WRITE(5,1050)
1050    FORMAT(/'$FILENAME FOR X,Y DATA:  ')
        READ(5,1060)LEN,FILEX
1060    FORMAT(Q,32A1)
        FILEX(LEN + 1)=0
```

```
      OPEN(UNIT=1,NAME=FILEX,FORM='UNFORMATTED',TYPE='NEW')
      DO 220 I=1,J
      READ(1) X(I),Y(I)
220   CONTINUE
      CLOSE(UNIT=1)
      CONTINUE
      RETURN
      END
```

APPENDIX E

DETERMINATION OF THE VOLUME OF A SAMPLE BY ARCHIMEDES' PRINCIPLE

An accurate method to determine the volume of a sample is by the use of Archimedes' principle. The volume of a sample at ambient pressure P_o and room temperature T_o (≈25°C) is given by

$$V(P_o, T_o) = \frac{\left(m_a - m_{H_2O}\right)\left(1 - \frac{\rho_a}{\rho_{wt}}\right)}{\rho_{H_2O} - \rho_a} \tag{E1}$$

To calculate the volume of a sample using Eq. (E1), one must determine the mass of the sample m_a in air, determine the mass of the sample in water m_{H_2O}, and use a known value of the density ρ_{H_2O} of the water, the density ρ_{wt} of the weights used on the balance, and the density ρ_a of the air in the room at the temperature T_o in the room. The masses in Eq. (E1) are apparent masses.

In this investigation, the masses m_a and m_{H_2O} were determined by using a Mettler Model H-311 Triple-Beam Balance, which has a maximum capacity of 240 g and is accurate to ±0.0003 g. Distilled water was used in this volume determination. It was deaerated, covered, and then cooled to 25°C. The density ρ_{H_2O} of the distilled water [17] and the density ρ_a of the air were, respectively, 0.99705 g/cm^3 and 0.001185 g/cm^3. An average from four volume determinations was taken

for both the butyl-252 sample and the type-W neoprene sample. Their volumes were, respectively, 8.8433 cm^3 and 8.7774 cm^3.

APPENDIX F

A FORTRAN PROGRAM (PYCNOM.FTN) TO CALCULATE THE SAMPLE VOLUME AS A FUNCTION OF TEMPERATURE AND PRESSURE

The FORTRAN program PYCNOM.FTN calculates the volume of the sample used in the acoustic pycnometer according to Eq. (14b). The listing of the program is given as follows:

```
C       THIS PROGRAM CALCULATES THE VOLUME AND THE ISOTHERMAL
C       BULK MODULUS AS A FUNCTION OF PRESSURE.
C
C       THIS PROGRAM STORES THE PRESS. AND VOLUME IN FILE
C       CALLED  'FOR002.DAT'
C
        BYTE ANS(4)
        DIMENSION A(14),AC(14),C(6),PRESS(100),VSAMP(100)
        1,DERIV(100),BULK(100)
        WRITE(5,1100)
1100    FORMAT(/,' $USE OLD DATA?')
        READ(5,1110,END=800)ANS
1110    FORMAT(4A1)
        IF (ANS(1).EQ.'N')GO TO 870
        OPEN(UNIT=1,NAME='PYCNOM.DAT',TYPE='OLD')
        READ(1,190)VO
        WRITE(5,195)VO
195     FORMAT(/,' V0=',F12.5)
        READ(1,190)TEMP
        WRITE(5,196)TEMP
196     FORMAT(/,' TEMP =',F12.5)
        READ(1,190)RHO
        WRITE(5,194)RHO
194     FORMAT(/,' RHO=',F12.5)
        READ(1,190)WTSR
        WRITE(5,198)WTSR
198     FORMAT(/,' WEIGHT OF HG FOR SAMPLE RUN =',F12.5)
        READ(1,190)WTCR
        WRITE(5,199)WTCR
199     FORMAT(/,' WEIGHT DURING CALIB. =',F12.5)
190     FORMAT(E12.6)
        READ(1,165)NUMCR
165     FORMAT(I2)
        DO 1200 K=1,NUMCR
        READ(1,1185)AC(K)
1185    FORMAT(E12.5)
1200    CONTINUE
        READ(1,197)NUMSR
197     FORMAT(I2)
        DO 1201 J=1,NUMSR
        READ(1,1199)A(J)
1199    FORMAT(E12.5)
1201    CONTINUE
        GO TO 1210
 870    OPEN(UNIT=1,NAME='PYCNOM.DAT',TYPE='NEW')
C       ALLOCATE STORAGE
        DO 10 J=1,100
                PRESS(J)=0.0
                VSAMP(J)=0.0
                DERIV(J)=0.0
                BULK(J)=0.0
 10     CONTINUE
C
        DO 20 I=1,14
                A(I)=0.0
                AC(I)=0.0
 20     CONTINUE
C
        DO 25 K=1,6
                C(K)=0.0
 25     CONTINUE
        WRITE(5,30)
 30     FORMAT(/,' $ENTER THE INITIAL SAMPLE VOLUME')
```

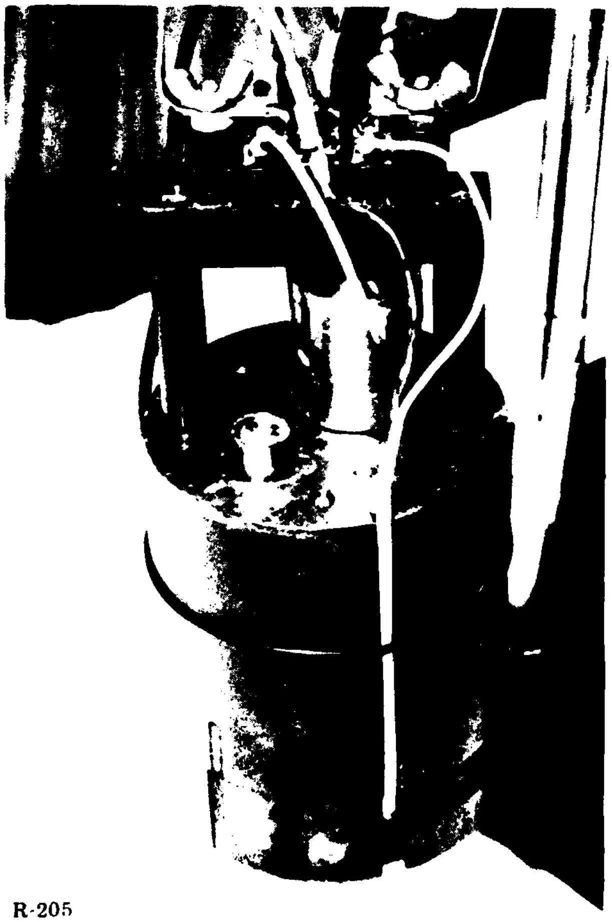
```
      READ(5,90)VO
      WRITE(1,290)VO
290   FORMAT(F12.5)
      WRITE(5,35)
 35   FORMAT(/,' $ENTER TEMP. OF SAMPLE RUN')
      READ(5,90)TEMP
      WRITE(1,291)TEMP
291   FORMAT(F12.5)
      WRITE(5,38)
 38   FORMAT(/,' $ENTER DENSITY OF HG')
      READ(5,90)RHO
      WRITE(1,292)RHO
292   FORMAT(F12.5)
      WRITE(5,40)
 40   FORMAT(/,' $ENTER WT. OF HG DURING SAMPLE RUN')
      READ(5,90)WTSR
      WRITE(1,293)WTSR
293   FORMAT(F12.5)
      WRITE (5,50)
 50   FORMAT(/,' $ENTER WT. OF HG DURING CALIBRATION')
      READ(5,90)WTCR
      WRITE(1,294)WTCR
294   FORMAT(F12.5)
 90   FORMAT(E12.6)
C     GET READY TO READ THE COEFFICIENTS
      WRITE(5,60)
 60   FORMAT(/,' $ENTER THE NUMBER OF COEFFICIENTS IN CALIB. FORMULA')
      READ(5,65)NUMCR
      WRITE(1,65)NUMCR
 65   FORMAT(I2)
      DO 95 J=1,NUMCR
              WRITE(5,80)J
 80           FORMAT(/,' $ENTER AC(',I2,')')
              READ(5,85)AC(J)
              WRITE(1,85)AC(J)
 85           FORMAT(E12.5)
 95   CONTINUE
      WRITE(5,96)
 96   FORMAT(/,' $ENTER THE NUMBER OF COEFFICIENTS IN THE SAMPLE RUN')
      READ(5,97)NUMSR
      WRITE(1,97)NUMSR
 97   FORMAT(I2)
      DO 98 K=1,NUMSR
              WRITE(5,99)K
 99           FORMAT(/,' $ENTER A(',I2,')')
              READ(5,101)A(K)
              WRITE(1,101)A(K)
101           FORMAT(E12.5)
 98   CONTINUE
1210  CLOSE(UNIT=1)
C     INITIALIZE VARIOUS VALUES TO ZERO
      VSNUM=0.0
      DVSNUM=0.0
      VSDEN=0.0
      DVSDEN=0.0
      VBSR=0.0
      TERM1=0.0
      TERM2=0.0
      DIFF=0.0
      CDEN=0.0
      DERIV1=0.0
      DERIV2=0.0
      VCNUM=0.0
      DVCNUM=0.0
```

```
      VCDEN=0.0
      DVCDEN=0.0
      TERMA=0.0
      TERMB=0.0
      FACTOR=0.0
      FACT1=0.0
      DERFAC=0.0
      VPT=0.0
      DERIV3=0.0
      VBCR=0.0
      P=0.0
      P2=0.0
      P3=0.0
      P4=0.0
      P5=0.0
      P6=0.0
      PINC=0.0
C     ENTER THE VALUES OF C(6)
      C(1)=0.1000E+01
      C(2)=0.1821E-03
      C(3)=-0.3753E-04
      C(4)=-0.519E-07
      C(5)= 0.454E-08
      C(6)= 0.119E-10
C     START PERFORMING THE CALCULATIONS
      TO=25.0
      CDEN=C(1)+C(2)*TO
      DIFF=(WTCR-WTSR)/RHO - VO
      FACTOR=DIFF/CDEN
      WRITE(5,120)
 120  FORMAT(/,' $ENTER MAXIMUM PRESSURE')
      READ(5,130)KP
 130  FORMAT(I4)
      WRITE(5,140)
 140  FORMAT(/,' $ENTER PRESSURE INCREMENT')
      READ(5,150)PINC
 150  FORMAT(F10.0)
C     INITIALIZE THE PRESSURE TO ZERO
      P=0.0
      JP=KP+1
C     ALLOCATE STORAGE
      DO 1500 J=1,JP
              PRESS(J)=0.0
              VSAMP(J)=0.0
              DERIV(J)=0.0
              BULK(J)=0.0
1500  CONTINUE
      DO 100 I=1,JP
              PRESS(I)=P
C             CALCULATE P2,P3,P4,P5,P6
              P2=P*P
              P3=P2*P
              P4=P2*P2
              P5=P3*P2
              P6=P3*P3
C     CALCULATE THE VARIOUS VOLUMES
C     CALCULATE VOLUME OF BORE FOR THE SAMPLE RUN
              VSNUM=A(8)+A(9)*P+A(10)*P2+A(11)*P3+A(12)*P4+
     1                 A(13)*P5+A(14)*P6
C     CALCULATE THE DERIVATIVE OF VSNUM
              DVSNUM=A(9)+2.0*A(10)*P+3.0*A(11)*P2+4.0*A(12)*P3
     1                 +5.0*A(13)*P4+6.0*A(14)*P5
              VSDEN=A(1)+A(2)*P+A(3)*P2+A(4)*P3+A(5)*P4+A(6)*P5
```

```
1                  +A(7)*P6
C       CALCULATE THE DERIVATIVE OF VSDEN
                DVSDEN=A(2)+2.0*A(3)*P+3.0*A(4)*P2+4.0*A(5)*P3+
1                  5.0*A(6)*P4+6.0*A(7)*P5
C       CALCULATE THE VOLUME OF THE BORE DURING THE SAMPLE RUN
                VBSR=VSNUM/VSDEN
C
                TERM1=VBSR/VSNUM
                TERM2=VBSR/VSDEN
C       CALCULATE THE DERIVATIVE OF VBSR
                DERIV1=TERM1*DVSNUM-TERM2*DVSDEN
C       START CALCULATIONS FOR CALIBRATION RUN
                VCNUM=AC(8)+AC(9)*P+AC(10)*P2+AC(11)*P3+AC(12)*P4
1                  +AC(13)*P5+AC(14)*P6
                DVCNUM=AC(9)+2.0*AC(10)*P+3.0*AC(11)*P2+4.0*AC(12)*P3+
1                  5.0*AC(13)*P4+6.0*AC(14)*P5
                VCDEN=AC(1)+AC(2)*P+AC(3)*P2+AC(4)*P3+AC(5)*P4+AC(6)*P5
1                  +AC(7)*P6
                DVCDEN=AC(2)+2.0*AC(3)*P+3.0*AC(4)*P2+4.0*AC(5)*P3+
1                  5.0*AC(6)*P4+6.0*AC(7)*P5
C       CALCULATE THE VOLUME IN THE BORE FOR THE CALIBRATION
                VBCR=VCNUM/VCDEN
C
                TERMA=VBCR/VCNUM
                TERMB=VBCR/VCDEN
C       CALCULATE THE CORRESPONDING DERIVATIVE
                DERIV2=TERMA*DVCNUM-TERMB*DVCDEN
C       CALCULATE THE VOLUME DUE TO A DIFFERENT FILL HEIGHT
                FACT1=C(1)+C(2)*TEMP+C(3)*P+C(4)*TEMP*P+C(5)*P2+
1               C(6)*TEMP*P2
                VPT=FACT1*FACTOR
C       CALCULATE THE DERIVATIVE OF VPT
                DERFAC=C(3)+C(4)*TEMP+2.0*C(5)*P+2.0*C(6)*TEMP*P
                DERIV3=DERFAC*FACTOR
C       CALCULATE THE SAMPLE VOLUME AND IT'S DERIVATIVE
                VSAMP(I)=VO+VBSR-VBCR+VPT
                DERIV(I)=DERIV1-DERIV2+DERIV3
C       CALCULATE THE COMPRESSIBILITY
                COMP=-(1.0/VSAMP(I))*DERIV(I)
C       CALCULATE THE ISOTHERMAL STATIC BULK MODULUS
                BULK(I)=1.0/COMP
C       INCREMENT THE PRESSURE
                P=P+PINC
 100    CONTINUE
C       WRITE OUT THE VOLUME AS A FUNCTION OF PRESSURE
        DO 200 J=1,JP
                WRITE(5,160)PRESS(J),VSAMP(J)
        WRITE(2,9999)PRESS(J),VSAMP(J)
9999    FORMAT(2E12.5)
160     FORMAT(/,' PRESSURE (MPA)=',E12.5,3X,'VSAMP (ML)=',E12.5)
C       WRITE OUT THE BULK MODULUS
                WRITE(5,170)PRESS(J),BULK(J)
 170    FORMAT(/,' PRESSURE (MPA)=',E12.5,3X,'BULK MOD. (MPA)=',E12.5)
 200    CONTINUE
        CLOSE(UNIT=2)
        WRITE(5,1000)
1000    FORMAT(/,' PROGRAM EXITS!')
        CALL EXIT
800     END
```

APPENDIX G

PICTURE OF ACOUSTIC PYCNOMETER AND ENGINEERING DRAWINGS



R-205

Fig. G1 — Assembled acoustic pycnometer

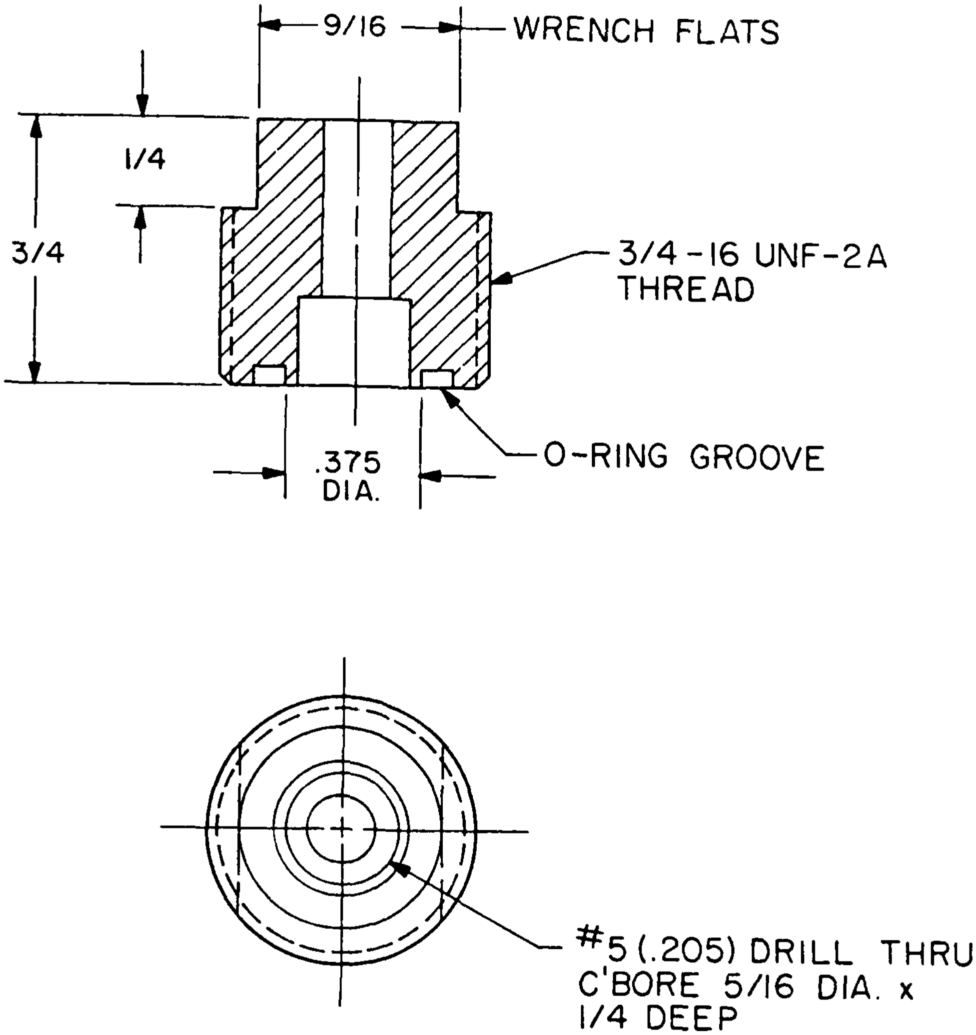


Fig. G2 — Thermistor plug

AD-A109 830 NAVAL RESEARCH LAB WASHINGTON DC F/G 14/2

A TECHNIQUE TO MEASURE THE VOLUME OF ELASTOMERS AS A FUNCTION O--ETC(U)

DEC 81 E K HOLMSTROM, A J RUDGERS

UNCLASSIFIED NRL-MR-4584 NL

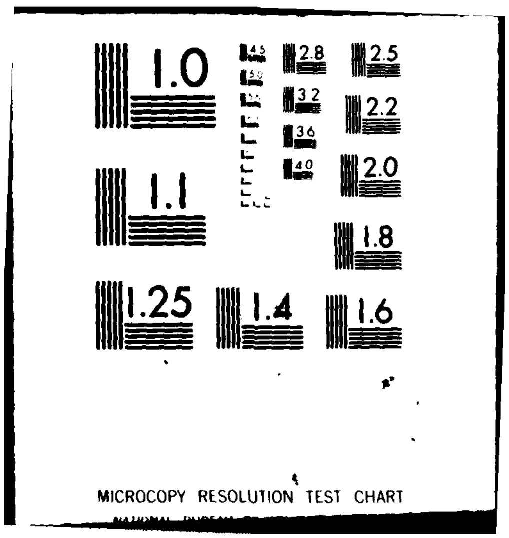
2 of 2

END

DATE FILMED

2-82

DTIC


1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6
MICROCOPY RESOLUTION TEST CHART

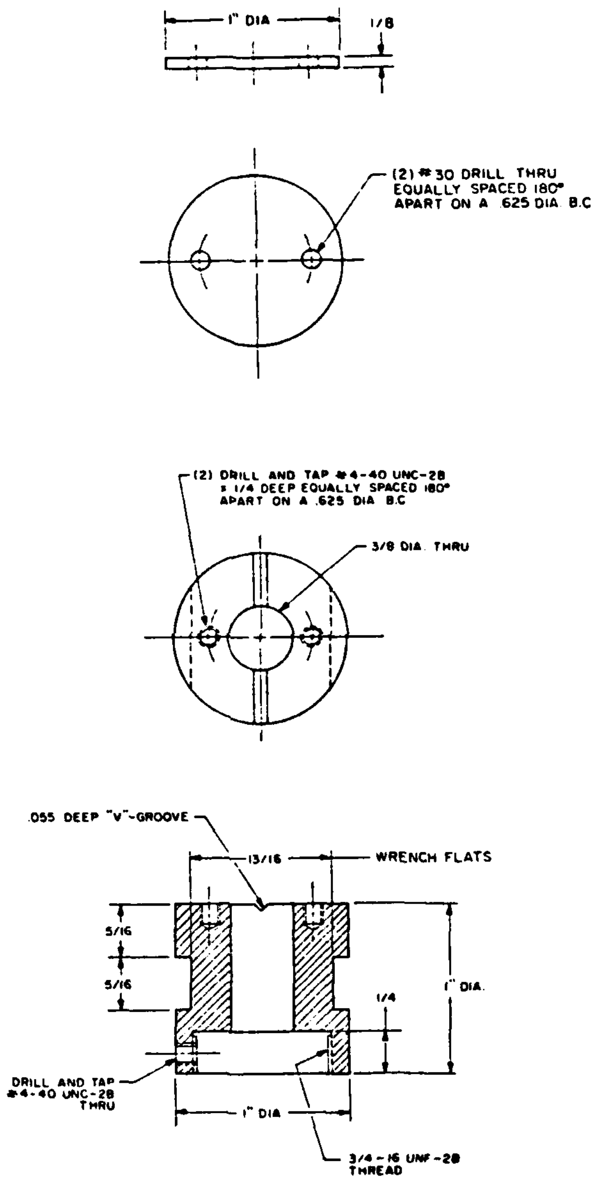


Fig. G3 — Thermistor-plug extension

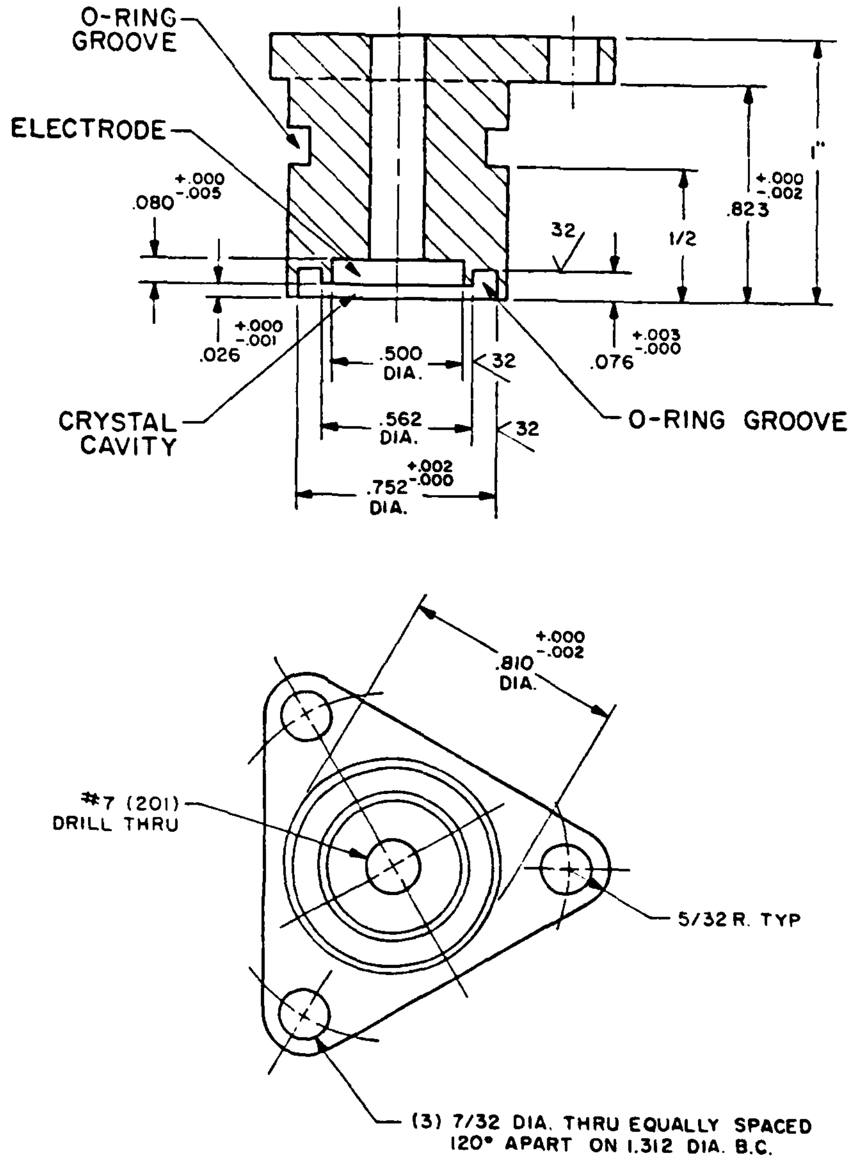


Fig. G4 — Pycnometer transducer mount

APPENDIX H

STATIC BULK MODULUS CALCULATION

The static bulk modulus of the elastomer samples used in the acoustic pycnometer measurement can be calculated from the least-squares coefficients obtained by fitting the experimental data to a sixth-degree polynomial. The sixth-degree polynomial expression for the volume of the elastomer sample as a function of pressure at constant temperature is given by

$$V_{SAMPLE} = A_1 + A_2P + A_3P^2 + A_4P^3 + A_5P^4 + A_6P^5 + A_7P^6 \qquad \text{(H1)}$$

where

A_1 through A_7 = the least-squares coefficients of the sixth-degree polynomial

The isothermal compressibility κ is obtained by taking the derivative of Eq. (H1) with respect to pressure and dividing this by the volume of the sample at the desired pressure. The isothermal compressibility is

$$\kappa = -\frac{1}{V_{SAMPLE}}\left(\frac{\partial V_{SAMPLE}}{\partial P}\right)_T . \qquad \text{(H2)}$$

The static bulk modulus B is the reciprocal of the isothermal compressibility κ. The expression used to calculate the static bulk modulus B at constant temperature is

$$B(P) = -\frac{\sum_{i=1}^{7} A_i \, P^{i-1}}{\sum_{i=2}^{7} (i - 1) A_i P^{i-2}} \quad . \qquad \text{(H3)}$$

The static bulk modulus of the butyl-252 sample at 10°C and 25°C is shown in Fig. H1. (The behavior of the curves above 65 MPa is believed to have no physical significance. This behavior seems to be an artifact of the least-square analysis).

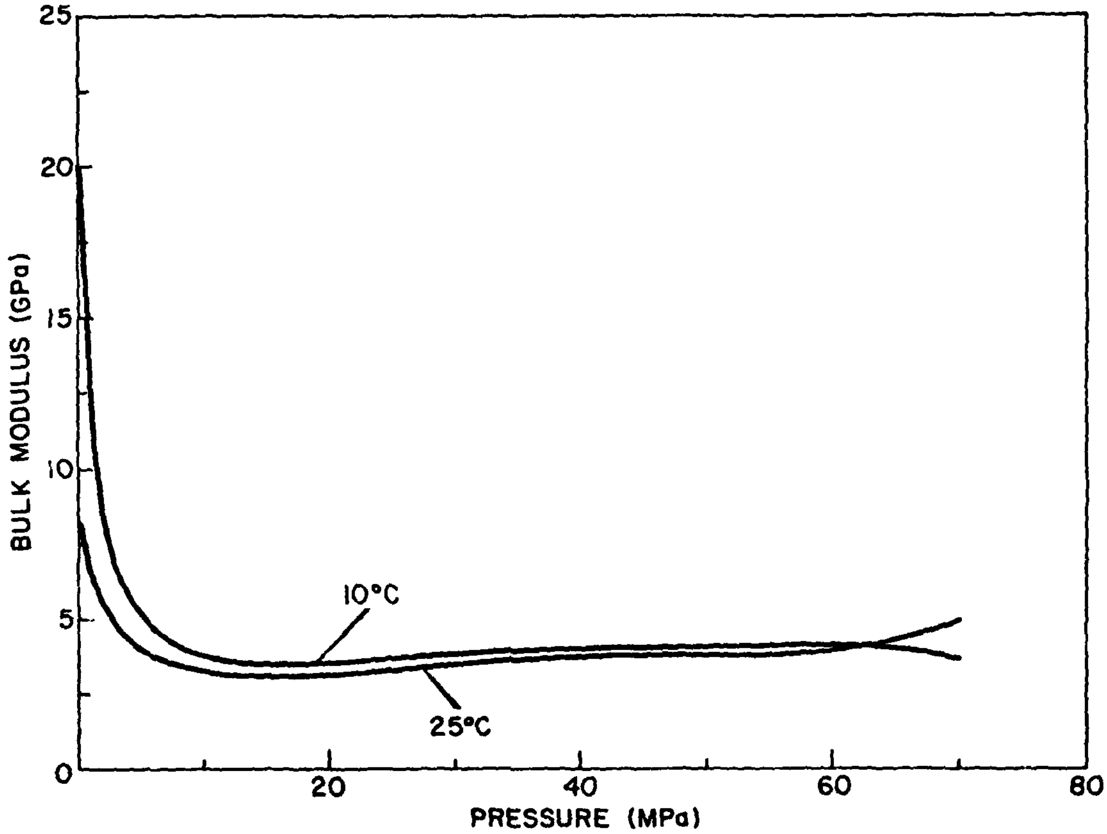


Fig. H1 — Static bulk modulus of butyl-252 at 10° C and 25° C

REFERENCES

1. R.J. Roark and W.C. Young, Formulas for Stress and Strain, New York: McGraw-Hill Book Co., 5th Edition, pp. 4, 1975.
2. R.J. Bobber, Underwater Electroacoustic Measurements, Washington, D.C.: U.S. Government Printing Office, pp. 312, 1970.
3. A.J. Rudgers, "Theory of a Method for Measuring the Complex Dynamic Bulk Modulus of Elastomers by use of Rayleigh-Scattering," Draft of NRL Formal Report to be published.
4. J.W.S. Rayleigh, The Theory of Sound, New York: Dover Publications, Vol. II, pp. 283, 1945.
5. R.D. Corsaro, J. Jarzynski and C.M. Davis, Jr., "Acoustic Densitometer with Results for Polyethylene Oxide," Journal of Applied Physics, Vol. 45, No. 1, pp. 1-8, 1974.
6. Ibid
7. Ibid
8. "CRC Handbook of Chemistry and Physics," R.C. Weast, ed., West Palm Beach, FL: CRC Press, Inc., 59th Edition, pp. F-11, 1978-1979.
9. E.G. Kimmich, "General Engineering Properties of Rubber," Chap. 4, Engineering Uses of Rubber, A.T. McPherson and A. Klemm, eds., New York: Rheinhold Publishing Corporation, pp. 72-100, 1956.
10. Ibid
11. Matec, "Special Instruction Manual for Using Model 122-B in Multiple Instrument System," Matec, Inc., Warwick, RI
12. Ibid

13. Ibid

14. H.M. Goodwin, _Precision of Measurements and Graphical Methods_, New York: McGraw-Hill Book Co., pp. 14-19, 1920.

15. Ibid

16. Ibid

REFERENCES NOT CITED

V.C. Anderson, "Sound Scattering from a Fluid Sphere," The Journal of the Acoustical Society of America, Vol. 22, #4, pp. 426, July 1950.

J.J. Faran, "Sound Scattering by Solid Cylinders and Spheres," The Journal of the Acoustical Society of America, Vol. 23, #4, pp. 405, July 1951.

P.M. Morse, Vibration and Sound, New York: McGraw-Hill Book Company, Inc., 1936.

S.N. Rschevkin, The Theory of Sound, New York: The Macmillan Co., Pergamon Press, Chapter 9, 1963.

R.W. Timme, "Sound Speed in Castor Oil," The Journal of the Acoustical Society of America, Vol. 52, #3, pp. 989, 1972.

DATE
FILME